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CENTER FOR CEMENT COMPOSITE MATERIALS

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The report describes the third year research activities of the Center and summarizes the overall achievements of the Center during the three year contract. The Center has produced very strong MDF cements and has made significant progress in enhancing the water resistance of the material. The important factors in controlling water sensitivity have now been identified and studies are in progress to quantify their influences. Cement hydration has been followed by a novel in-situ technique involving nuclear magnetic resonance. Fiber-matrix interactions in MDF laminates were also studied. Characterization of DSP pastes have shown that the matrix is microporous; mesopores are absent unless the material is allowed to dry out. This results in water adsorption at low relative humidities, which adversely impacts on electrical properties. DSP pastes are a good insulating, low dielectric material as long as it is kept dry.

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Hydration under autoclaving conditions may be a way of solving the problem and hydration chemistry at various temperatures have been studied. The Center has also studied a magnesium triphosphate cement, as a precursor to polyphosphate cements and is exploring inorganic-polymer composites at the molecular levels. Finally the Center has investigated the influence of packing and particle interactions on the rheology of suspensions with high solids contents.

The Center also established and maintains a facility for the characterization of powders and porous materials. This facility is available to other research groups in the University. The Center is now affiliated with the NSF Center for the Science and Technology of Advanced Cement-Based Materials.

Contract: F49620-87-C-0023

CEMENT PASTE MATRIX COMPOSITE MATERIALS CENTER

Final Report

submitted to

U.S. Air Force Office of Scientific Research
Bolling Air Force Base
Washington D.C.

Prepared by: J. F. Young

January 1990
Department of Civil Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801

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Summary

This report describes in detail the research progress in the Center during the third and final year of the contract. It also summarizes the overall achievements of the Center. The following are highlights of the Center progress.

- MDF cements with dry strengths in excess of 280 MPa and wet strengths (after 14-day soak) in excess of 150 MPa can be prepared routinely using organotitanate coupling agents.

- Water is adsorbed by MDF cements through a molecular diffusion process which swells and softens the polymer matrix. This is followed by hydration of the calcium aluminate cements which creates an alkaline environment.

- Ionic cross-linking is important in developing the properties of the material, but if it is too rapid has a detrimental effect on processing. Processing flaws will reduce strength, but has a disproportionate effect on wet strengths.

- The development of polymer-polymer interfaces, that might occur during the processing of MDF cements, have been investigated in terms of the dynamics of inter-diffusion of polymer chains and fractal analysis. A modified single chain reptation dynamics approach seems to give a good description of the interface structure.

- MDF cements cannot be processed with the addition of short fibers as reinforcement, since the fibers are damaged by roll-milling. Fiber arrays can be laminated between MDF sheets. SiC fibers show good bonding with the matrix, even when treated with stearic acid as a bond breaker a value of 2 MPa was measured, which is higher than most values measure for fibers embedded in conventional cement pastes.

- DSP cement paste develop a sufficiently dense matrix that only micropores are present in a properly processed, well-cured material. Much of this porosity is accessible only to water. When subsequently dried a portion of the porosity is converted to larger mesopores.

- Only about one third of the cement reacts in a well-cured DSP cement paste, resulting in cement grains acting as a microfiller. The microsilica component reacts gradually over several months, but because of the intrinsic microporosity of the binder a compressive strength limit of about 30,000 psi is reached.

- DSP cements act as insulating, low dielectric materials, with hollow spheres used as fillers K' values approaching 4 can be obtained. However the micropore system results in a pronounced degradation of electrical properties after exposure to even low relative humidities.
- Magnesium oxide-ammonium dihydrogen triphosphate ion produce a strong cement in which the triphosphate moiety is retained. The cement shows a gel-like rheology prior to hardening, but can be compacted to form a dense body.
- Crystalline calcium aluminate hydrates, which contain polymeric molecules, have been prepared by precipitation from saturated solutions containing dissolved polymers. The influences of the polymers on the rate of crystallization, phase composition and phase stability has been elucidated. Preliminary results suggest that when these crystals are intermixed with a calcium aluminate cement a stronger matrix is created.
- Suspensions of uniformly sized particles adopt an ordered packing when particle volume fractions approach 0.60, forming a stiff gel. The response of this gel to increasing shear strength varies from elastic to viscoelastic behavior. A sharp decrease in viscosity is observed as the particle order is destroyed.
- The Center has established an instrumental facility for characterization of powders and porous materials. In addition to supporting Center projects,t he facilities has been used by other research groups on the campus and by industrial affiliates.
- The Center has affiliated with the NSF Center for the Science and Technology of Advanced Cement-Based Materials. The industrial affiliates program has been transferred to this Center.

1. Introduction

This report summarizes the technical progress that occurred during the last year of the contract: from October 1 1988 to October 31 1989. It also summarizes the overall achievements during the life of the contract.

The original aims of the Center were quite ambitious, namely to create a strong interdisciplinary program to examine the potential of using cementitious reactions to create new ceramic-like materials. This required the development of a comprehensive and coordinated research program to investigate microstructure-property relationships, as well as an understanding of the chemical and physical makeup of these materials. It became clear early on in the program that processing was a key element for several of the projects, and that, until reliable processing procedures could be developed fundamental studies would not progress satisfactorily. We now recognize the importance of processing science in this area and future plans call for some specific research projects on this topic.

The Center has indeed developed a broad program that involves a wide range of disciplines. Faculty have expertise in cement science, ceramic science, polymer science, inorganic chemistry, mineral science and colloid science. Likewise graduate students come from a broad range of programs, majoring in ceramic engineering, materials science and engineering, chemical engineering and geology. It has taken time for these investigators to become familiar with the existing knowledge concerning cement chemistry and physics and the specialized experimental methodologies used to study these systems.

Additionally it should be remembered that the first year of the contract concentrated on acquisition of state of the art instrumentation, with the result that most of the research projects did not get underway until the second year. Thus most projects have been active for just over two years.

As a result of these three factors the tangible products of the contract, in terms of papers published in technical journals, have been less than would be expected form an ongoing program. However, several of the project investigators have indicated that papers are being readied for submission to journals over the next six months. Moreover, participants have given many presentations at technical meetings describing the ongoing work and the preliminary findings. It is clear that the program at Illinois is widely recognized and it continues to attract attention. This recognition was undoubtedly an important factor in the award a year ago of a NSF Science and Technology Center for Advanced Cement-Based Materials. Although the Center is administered by Northwestern University, the faculty in the Center for Cement Composite Materials play a major role in the new Center. Professor Young serves as the Associate Director of the NSF Center.

Several of the projects started with Air Force funding will continue in the new center. Additional faculty at Illinois have joined the group, indicating that the Center has attracted the interest of its professional colleagues.

The Center has also increased support from the University. During the past year additional money was provided by the administration for further instrument acquisitions. The heads of the Departments Civil Engineering and Materials Science and of Engineering enthusiastically support the Center, and publicize it as an important part of the research activities of the respectiv Departments.

In the following pages a detailed description of research progress over the past year is provided for each project. The overall achievements of the whole program for the full three year period are then summarized.

Table 1 - Summary of Research Projects

Project #	Title of Project	Principal Investigators	Faculty Associates	Research Assistants	Start Date	Project Funding*
21	MDF Cement Processing and Properties	M. Berg, J. F. Young	R. Wool	P. Russell, R. Desai, R. Falkner, J. Shunkwiler	10/86	$68,000
22	Electrical Properties Cements+	D. A. Payne, J. F. Young		D. Leigh	Completed 1988	
23	Fiber/Matrix Adherence	J. Homeny, S. D. Brown		D. Hansen, A. Burreson	6/87	$53,000
24	Intercalation of Polymer in Inorganic Crystals	S. I. Stupp		P. Messersmith	8/87	$47,000
25	Polymer-Solid Interactions	S. Granick			Cancelled 1988	
26	Polymer-Cement Interfaces	R. P. Wool		H. Zhang	8.87	$27,000
27	Phosphate-Bonded Cements	W. G. Klemperer	J. F. Young	M. Wagner^	6/87	$32,000
28	High Strength Cement Pastes	R. L. Berger, J. F. Young		G. K. Sun^, S. Touse++, T. Bier^	8/87	$26,000
29	Setting Processes for Cements	C. F. Zukoski		L. B. Chen	6/87	$29,000
30	NMR Study of MDF	R. J. Kirkpatrick		X. D. Cong	8.88	$5,000

*10/1/88-10/31/89
+Project completed 8/88

++Not supported by Center funds
^Research Associates

2. Research Programs

Table 1 summarizes the projects that were funded during the past year. Budget reductions for the final year (a cut of about 12%) were accommodated by terminating two projects. One, on electrical properties, had achieved its initial objectives and the student working on it graduated. The other, on polymer-solid interactions, had not progressed satisfactorily due to inadequate staffing. The remaining projects were continued from the previous year.

2.1 Project #21 - MDF Cement Processing and Properties

The objectives of this project have been to improve the mechanical strength and water resistance of macro-defect-free (MDF) cements.

Control of cross-linking during processing: Although high strengths up to 300MPa were reported last year there has been concern about reproducibility of strengths from the same formulation. Control of temperature rise in the material during compounding on the two-roll mill is an important parameter. A water chiller was purchased enabling the rolls to be cooled down to 10 C and this has successfully reduced heating of the material during processing. However, "overworking" of the material during processing can still occur even at the lower operating temperatures, and this apparently leads to surface defects [e.g. "tears"] and lamination defects during the calendering step. These defects may have a disproportionate influence on the wet strength of the composite after prolonged soaking.

Studies using Portland cement have shown that the rate of crosslinking and insolubilization of the polyvinylalcohol (PVA) are critical to achieving high flexural strength. This process begins as soon as initial blending is started. Overworking of the material will occur if the material reacts too rapidly with the cement so that the PVA gel starts to stiffen before the high shear mixing and calendering is completed. Portland cement is a calcium silicate cement and does not provide a high concentration of aluminate ions in solution, as does calcium aluminate cement. [It is thought that the aluminate ions is an effective crosslinking specie.] Instead, Portland cement releases high concentrations of calcium ions and hydroxide ions. The solution approximates to a saturated solution of calcium hydroxide. The pH reaches about 12.5, which is higher than that attained in the calcium aluminate cement system (11.5). The high pH will: (1) increase the rate of

hydrolysis of the residual acetate groups on the PVA, thereby decreasing the solubility of PVA, and (2) increase the binding capacity of calcium ions with PVA due to partial ionization of the hydroxyl groups. Consequently a more rapid reaction between the cement and the polymer is observed in the PVA-Portland cement system. This lead to gross lamination defects which become strength limiting flaws. The flaws can be minimized by controlling the calcium ion concentration using EDTA to complex part of the calcium. However, it appears that a certain pH is needed to enhance calcium cross-linking. When pure dicalcium silicate was used in place of Portland cement, a strong composite could not be obtained. A summary of relevant experiments is given in Table 2.

Table 2 - Compositions of solution in contact with Portland cement and related systems (w/c = 0.20)

System	5 min values		30 min values	
	$[Ca^{2+}]$mM	pH	$[Ca^{2+}]$mM	pH
Calcium Aluminate Cement (Secar 71)	7.5	9.2	8.0	10.9
Portland Cement (Type I)	17	10.9	18	12.3
Tricalcium Silicate (Synthetic)		11.0		12.6
Dicalcium Silicate (Synthetic)		1.0-0		11.6

New Processing Methods for MDF Materials: New processing methods are being explored using a Brabender mixer where the torque and temperate of mixing can be accurately monitored. The object of this work is to obtain more intimate mixing of the PVA with the cement particles and potentially eliminate compression stages in processing necessary to remove bubbles and voids from the early stage blend. Success in this effort would allow considerable flexibility in processing of MDF materials with polymer processing extrusion and molding technology. The optimal method for mixing fine powder cement particles with more coarse PVA particles is being explored. This technique also allows us to investigate several additives and polymer blends which are expected to improve properties in a manner predicted by the percolation theory.
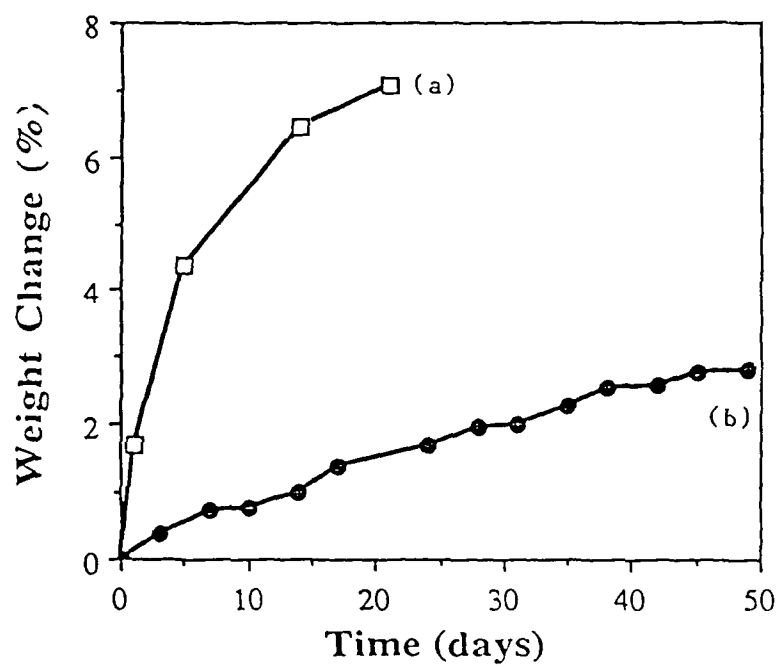
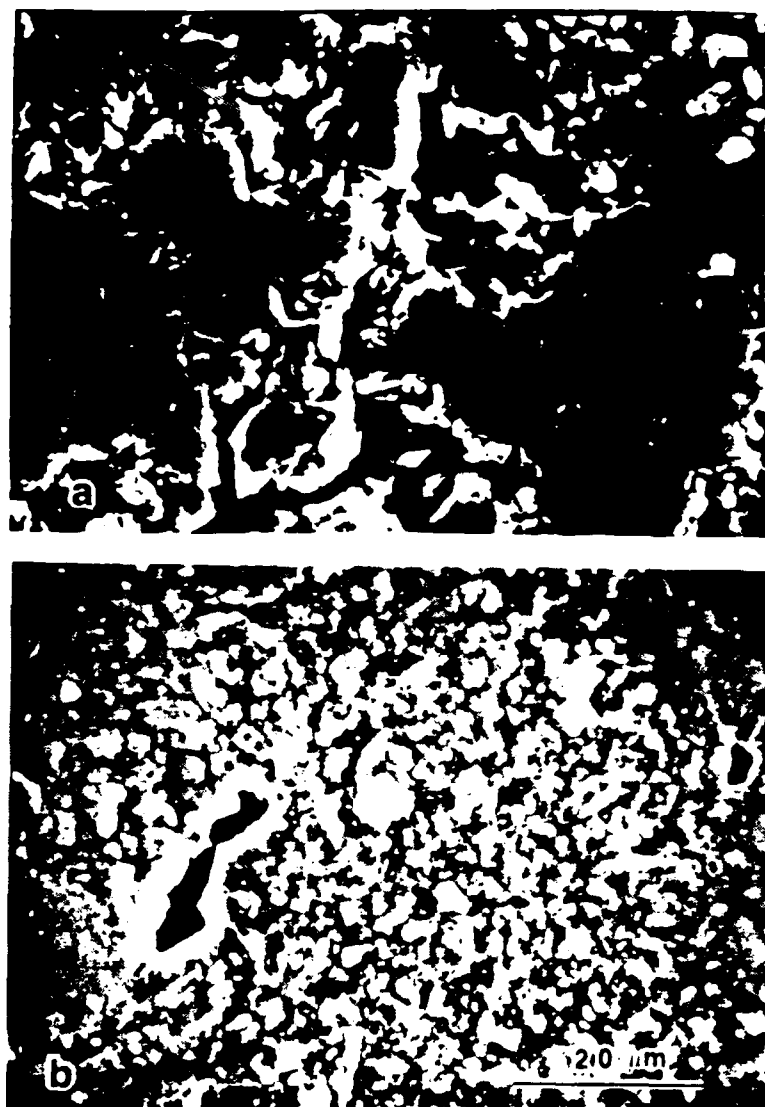Figure 1. Moisture absorption of two different preparations of MDF cement.

Figure 2. Surface textures of the two MDF cement preparations
for which moisture adsorption is given in Figure 1.

Kinetics of moisture uptake: Results continue to suggest that the PVA matrix is adsorbing moisture causing it to soften and swell, which in turn reduces the flexural strength. In addition, further hydration of the cement occurs. In static immersion tests this raises the pH of the contact solution to 11.0-11.5 which is sufficiently alkaline to attack the PVA. Monitoring the pH rise is a useful non-destructive method of monitoring water resistance.

The rate at which moisture is taken up (Fig. 1) appears to be sensitive to the condition of the surface of the bulk material (Fig. 2). The rate of moisture uptake is linear with the square root of time which indicates a molecular diffusion controlled process. Limited take up of moisture can have interesting consequences. In one set of experiments MDF cement samples were cycled between 0% and 100% r.h. at 7 day intervals. During this time about 15-20% of the total moisture uptake was observed. Strength tests on random samples at the end of each cycle showed that strengths were higher at the end of the wet cycle, and lower at the end of the dry cycle. This apparent contradictory result can be explained by the diffusion process. At the end of the wet cycle only a thin layer of the PVA matrix on each surface will have fully adsorbed moisture, causing swelling and softening. The interior will remain dry, hard and strong and will tend to resist the swelling at the surface. This will put the surface into compression so that on loading a higher tensile stress will be required to initiate fracture. On drying the surface will shrink under restraint from the core and develop tensile stress at the surface. The polymer again becomes more brittle so that it is possible that some surface cracks may also form. Both these effects will act to reduce the measured flexural strength.

Enhancement of water resistance: Previously, experiments were reported that showed some improvements when other cross-linking agents used for PVA films, or metallo-organic coupling agents were used. These approaches have been further explored.

Heat treatment of PVA films at temperatures above 100 C are known to improve water resistance. This is attributed to enhanced intermolecular interaction between chains through improved hydrogen bonding. This can be viewed as an increase in the degree of crystallization, since chains must adopt more aligned configurations for stronger bonding to occur. It can be considered a form of cross-linking. The approach was tried for MDF cement by increasing the temperature of pressing prior to final curing. The dry flexural strength and the subsequent wet strength were both improved, as shown in Figure 3. However, above 120 C the values tend to decrease, and this regression is attributed to alkaline degradation of the polymer. Thus, the improvements that can be realized by this strategy are quite limited.
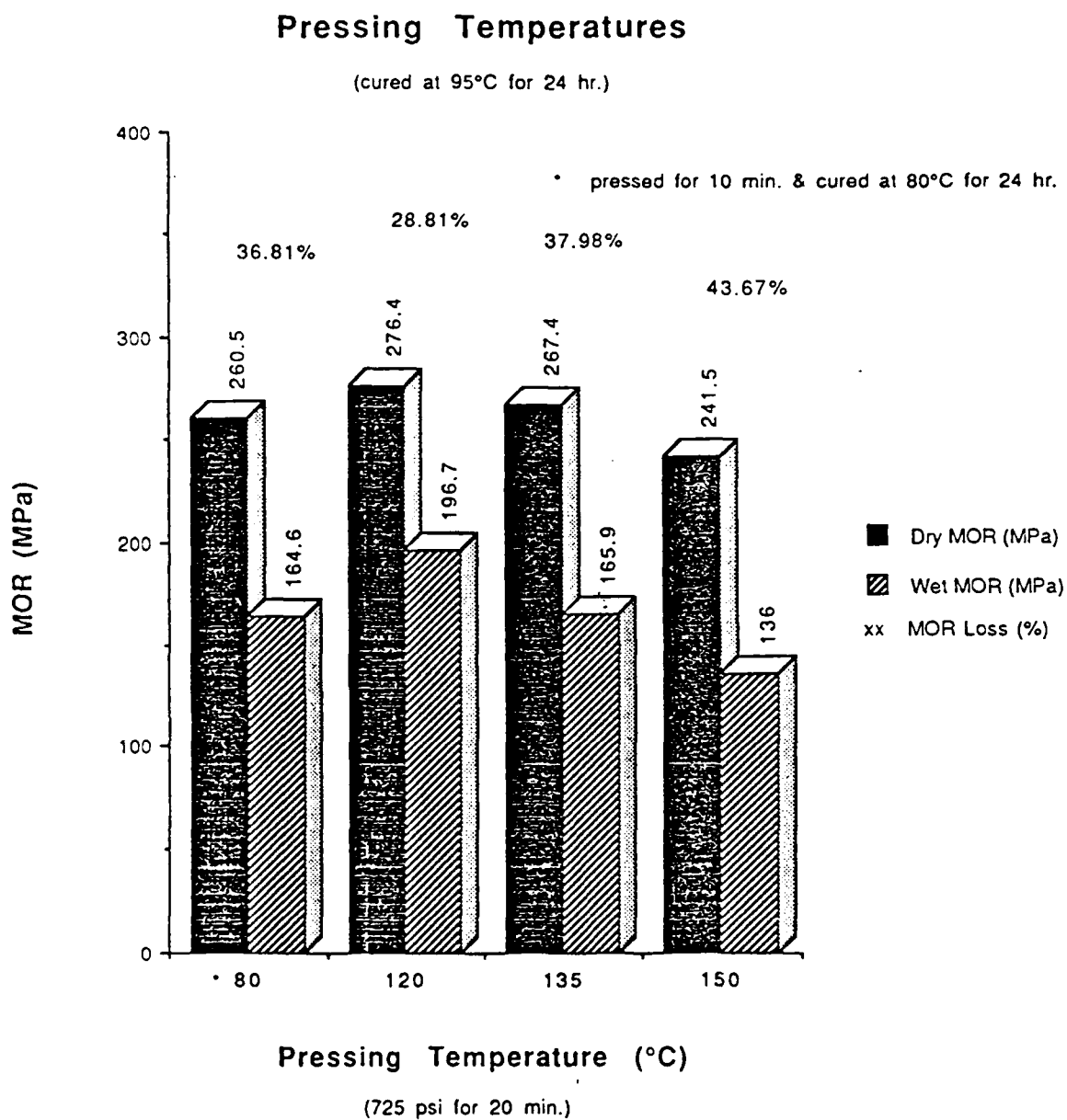
Pressing Temperatures

(cured at 95°C for 24 hr.)

Figure 3. Effect of pressing temperature on the wet and dry strengths of MDF cement. (Pressed at -725 psi for 20 minutes at temperature shown, followed by drying at 95°C for 24 hrs.
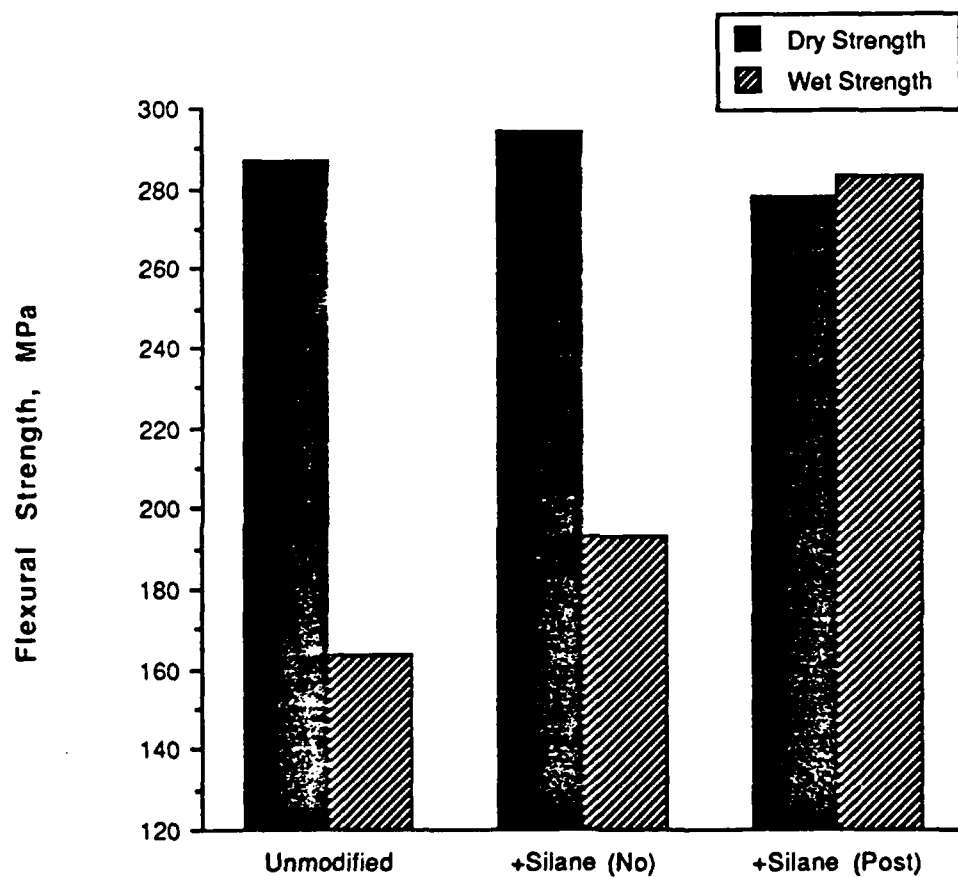
Figure 4. Influence of a silane coupling agent on the wet and dry strength of MDF cement (NO = no change in processing; POST = a subsequent exposure to high humidity to enhance silane polymerization).
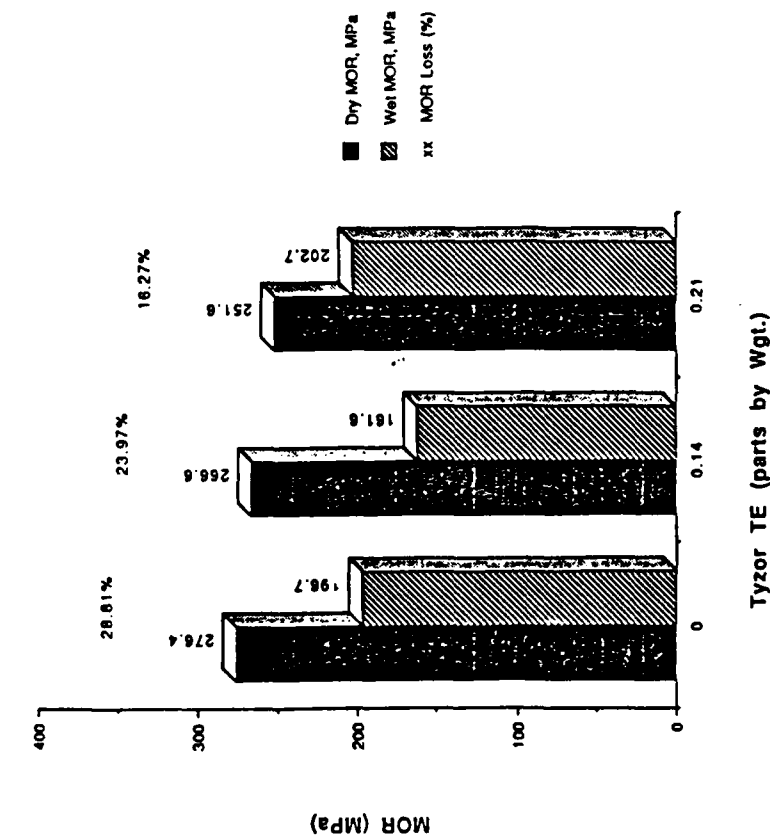
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Figure 6. Comparison of improvement in the moisture sensitivity of MDF cements.

Figure 5. Effect of organotitanate on moisture sensitivity of MDF cement (pressed at 725 psi/120°C for 20 minutes and dried at 95°C for 24 hrs.).
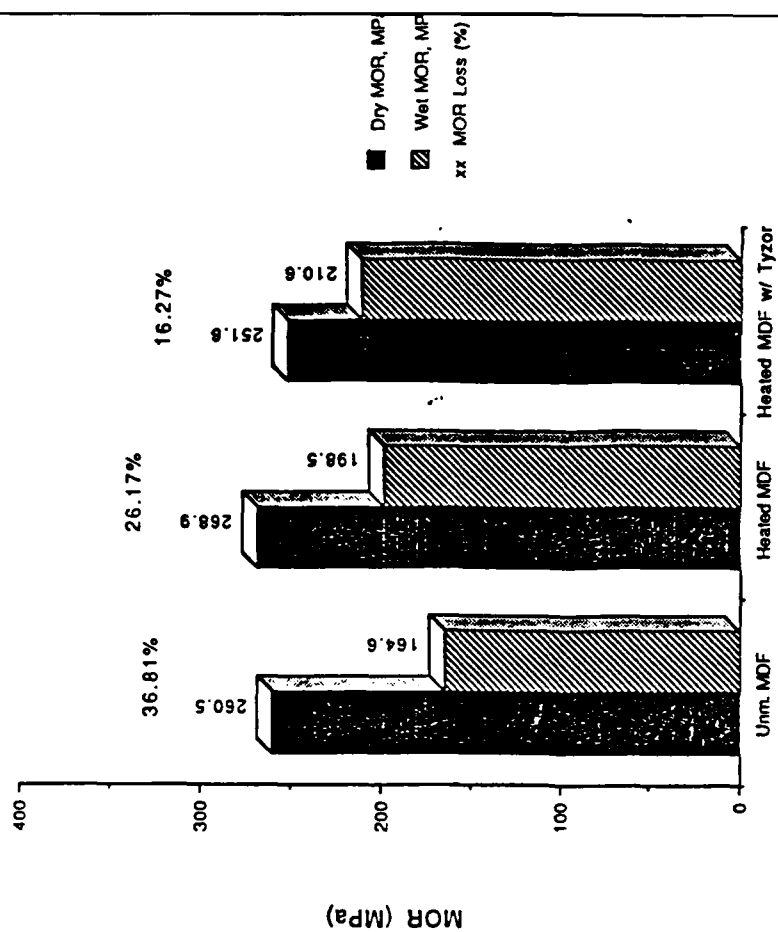
Further work was continued with the addition of the epoxy-functional silane coupling agent that was reported on last year. It was observed that on immersion in water an oil was slowly released from silane-treated samples. It appears that only partial polymerization of the silane is occurring, so that the full coupling action between cement and polymer will not be realized. Thus a strategy was devised to overcome this problem. Subsequent to the final cure, the composite is exposed to 95% r.h. at 50 C for several days, to allow for further polymerization and reaction between the epoxy groups of the silane and the hydroxyl groups of the PVA. By this means we have achieved very favorable results (see Figure 4), but it has not been possible to regularly achieve this level of performance. Three factors may be operating: (1) lack of uniform distribution of silane throughout the composite, (2) a rapid rate of initial hydrolysis under high pH conditions, which is difficult to control, and (3) a slow rate of subsequent polymerization and reaction with hydroxy groups at high pH.

Various coupling agents other than the silanes have been evaluated. The only compound to show more promising results is a triethanolamine titanate chelate [Tyzor TE, Dupont]. This compound has some very attractive feature as a coupling agent for cement systems. It permits cross-linking to take place only when the temperatures raised above 100 C, and it is stable at high pH, only hydrolyzing slowly in the presence of water. Figure 5 shows the improvements that can be attained using Tyzor TE; only a 17% decrease in strength is observed after a two week immersion in water. Further improvements appear possible by optimizing the processing variables and determining more precisely the basic mechanisms operating in these systems.

It should be noted that dry flexural strengths in excess of 250 MPa can be consistently obtained, and that wet strengths in excess of 200 MPa are possible. These values should be compared with the figures reported by ICI when this project started of 150-200 MPa for dry flexural strengths. A summary of reproducible achievements is given in Figure 6. In reaching this level of performance we have acquired a better, but still incomplete, understanding of the cement-polymer interactions.

2.2 Electrical Properties of Cements

This project was completed in 1988. It was shown that cement-based materials (both MDF and DSP cements) had excellent dielectric properties in the dry state. However, in the presence of moisture, a significant degradation of properties occurs as water enters the matrix and decreases its electrical resistivity. The problem is most acute for DSP cements which have connected porosity. Results are summarized in Table 3.

Table 3 - <u>Electrical Properties of Cementitious Materials</u>

Material	RH (%)	Resistivity (ohm.cm)	Dielectric Constant (K')	Dielectric Loss (tan δ)
DSP Cement Paste				
	0	5×10^{10}	5.2	0.02
	50	3×10^{8}	14	0.18
	100	4×10^{7}	22	0.29
Paste with fillers				
+ quartz	0	--	6.2	0.02
+ hollow spheres	0	--	5.5	0.01
+ boehmite	0	--	5.0	0.01

2.3 Fiber-Matrix Adherence

Objective: This project is studying the effect of fiber surface modification on the adherence of fibers to the MDF cement matrix.

The success of composite materials in engineering applications lies in their ability to transfer stress from less rigid materials (matrices) to those of higher moduli (fibers). This stress transfer mechanism, which is a function of the nature of the interface, is one limiting factor in determining the mechanical behavior of the composite. Therefore, the primary objective of this research is to understand the effects of fiber surface treatments on the adherence of fibers to the MDF matrix and correlate the nature of the interface to the mechanical performance of the composite. This broad based approach entails the following:

(1)   Perform various fibers surface treatments and incorporate these fibers into aligned fiber/MDF matrix composites.

(2)   Characterize the fiber surface chemistry using ESCA and Auger Electron Spectroscopy (AES).

(3)   Evaluate the strength of the fiber/matrix bond via indentation techniques on single fibers in the matrix.

(4)   Characterize the nature of the interfacial zone using electron microscopy.

Surface Modifications: The composite system consists of Nicalon (Nippon Carbon Co. Ltd.) SiC fibers reinforcing an MDF matrix. Seven separate fiber surface modifications were performed on the SiC fibers with the intent of varying the fiber/matrix adhesion. The fibers in each case were first heat treated in an oven to remove the protective epoxy sizing. A summary of surface treatments is shown in Table 4.

Table 4 - Fiber Surface Modifications

Fiber Treatment	Description
1000-Air	1000°C in air for 1 hrs.
1000-Oxygen	1000°C in oxygen for 1 hr.
1000-Nitrogen	1000°C in nitrogen for 1 hr.
1000-Argon	1000°C in argon/10% H_2 for 1 hr.
Stearic Acid	Coating of many monolayers from solution.
Silane	Dow Cornings Z6040 epoxy silane coupling agent.
1000-Air/Silane	Z6040 silane coating on 1000-Air treatment.

Fiber surface chemistry was characterized using ESCA and AES facilities at the Oak Ridge National Laboratory (ORNL), Materials and Chemistry Technology Department. ESCA was used to obtain quantitative elemental analyses of fiber surfaces. Broad scans were obtained showing the predominant peaks (i.e. Si, C and O) and regions around peaks of interest were expanded and integrated to obtain the relative amounts of each element. Chemical bonds were assigned to measured binding energies based on standard references. AES was utilized to depth profile fiber surfaces to obtain relative elemental concentrations with sputter depth.

The predominant compounds for all fiber surfaces from ESCA analysis included relative amounts of carbon, silicon dioxide and various hydrocarbons from C-C, C-H and Si-O bonds. Auger results showed the relative thickness of the oxide layers and surface coating, as elemental compositions were traced form the fiber surface to the bulk. Characterization results indicated that the heat treatments successfully altered the fiber surface chemistry while only slightly affecting the bulk chemical composition. In oxidizing the atmospheres, carbon was stripped form the surface and replaced by oxygen changing

surface chemistry while only slightly affecting the bulk chemical composition. In oxidizing the atmospheres, carbon was stripped form the surface and replaced by oxygen changing the surface from silicon-oxygen-carbon species to silicon-oxygen species. In reducing atmospheres, the surfaces were carbon-rich with various hydrocarbon species.

Fiber Matrix Bonding: Composite specimens were prepared by laminating a 2-D array of aligned fibers between two sheets of MDF cement at 1000 psi at 80°C. The MDF formulation was slightly modified to improve lamination (100 parts of cement, 9 parts of polymer and 12 parts of water by weight). Properties of the fiber/matrix interface, determined on composite fabricated utilizing the modified fibers, were generated from load-displacement data via microdebonding tests on a Nano-Indenter System at the ORNL Mechanical Properties User Center. Figure 7 shows a schematic diagram of the indentation experiment modelled by Marshall and Oliver, in which a pyramidal indenter pushes on the cross section of fiber within the matrix to initiate debonding/frictional sliding at the interface. The total displacement of the indenter, u_T, is the sum of the sliding distance, u, and the penetration of the indenter into the fiber, u_O, from elastic and plastic deformation.
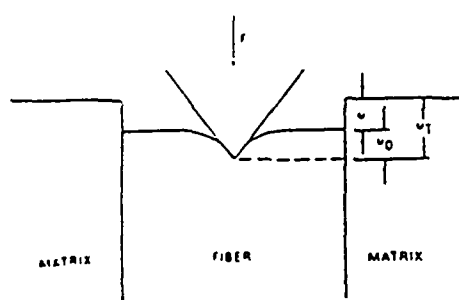
$$U_T = U_o + U$$

U_T = total displacement

U_o = elastic + plastic deformation

U = true sliding displacement

MATRIX   FIBER   MATRIX

Figure 7. Schematic diagram of indentation experiment.

Indentation results correlate the mechanical performance to the fiber surface chemistries. Figures 8 and 9 are load-displacement curves of the two systems that have been successfully analyzed to date for interfacial shear strength, τ_i. The solid line in these curves is the calibration curve used to correct for the plastic deformation of the indenter into the fiber. By subtracting this curve point for point from the total displacement curve to the right of it, the true fiber sliding displacement is obtained, as shown in the far left curve.

In the fabrication of the composite system with fibers subjected to the stearic acid treatment, it appeared that debonding occurred around 40 mN followed by frictional sliding. The composite system fabricated with fibers subjected to the 1000-argon treatment, however, revealed very little fiber/matrix adhesion, as it appeared that sliding began at very low loads. Frictional sliding, in this case was characterized by a decreasing slope in the loading curve followed by hysteresis in the unload/reloading curves.

According to Marshall's analysis, fiber sliding entails both extension of a debonding crack at the fiber/matrix interface, followed by frictional sliding over the crack surfaces. The sliding depth is governed by the length, c, of the debond crack. The appropriate equations and model are shown in Figure 9a.

By manipulating the top equation into the form of $(Stress)^2$ vs. displacement, which predicts linearity in the first loading, a line may be fitted to the data to obtain the slope and allow for the calculation of τ_i, with the known radius and modulus of the fiber, as shown in Figure 9b. The interfacial shear strengths for the systems studied are shown in Table 5. To date, the analysis for the calculation of the interfacial shear strength has been completed for the above systems. The composite systems fabricated with fibers subjected to 1000-Nitrogen and 1000-oxygen treatments are in progress. The values so far attained a higher than those measured for fibers embedded in conventional cement pastes.

Table 5 - Interfacial shear strengths

Composite System	τ_i(MPa)
100-Air	*
1000-Argonne	2.0
Stearic Acid	4.4
Silane	*
1000-Air/Silane	*

*Shear strength greater than can be determined using present equipment.
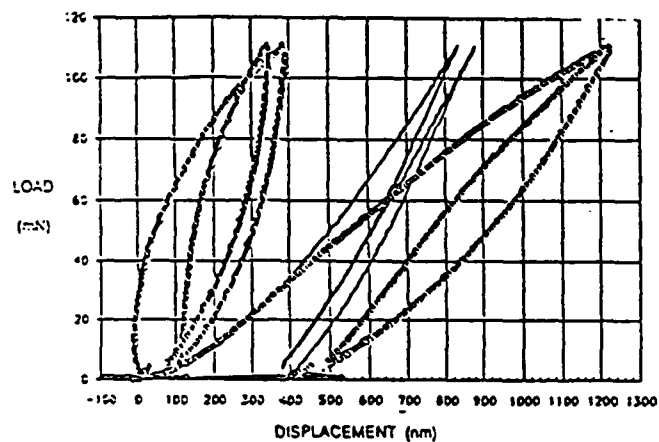
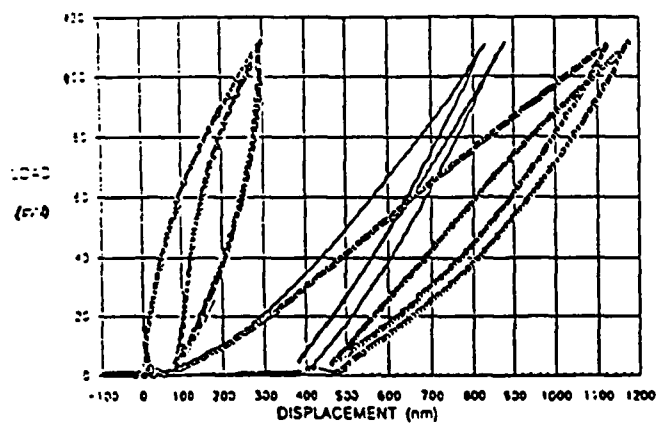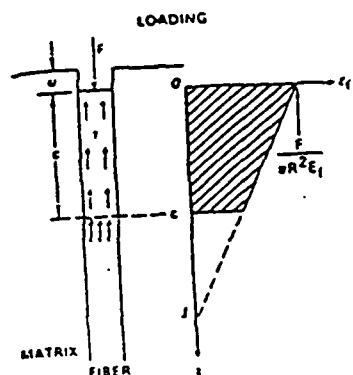Figure 8a. P-u curve for the stearic acid composite system.

Figure 8b. P-u curve for the 1000-argon composite system.

$$u = \frac{F^2}{4\pi^2 R^3 \tau E_f} - \frac{2\Gamma}{\tau}$$

$$(Stress)^2 \frac{R}{4} = \tau E_f u + 2\Gamma E_f$$

Figure 9a. Model of interfacial debonding and frictional sliding.

1000ARGON: y = -3.8031e+4 + 3523.7x

STEARIC ACID: y = 6.3023e+4 + 1636.5x
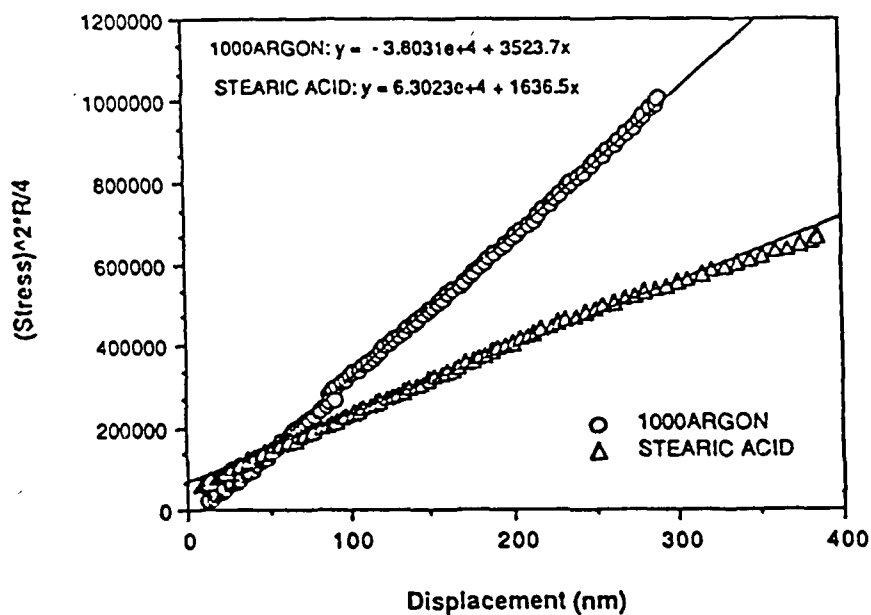
O 1000ARGON
△ STEARIC ACID

(Stress)^2*R/4

Displacement (nm)

Figure 9b. (Stress)^2 vs. displacement plots.

Table 6. Polymers used in the study of organoceramics.
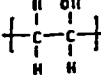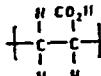
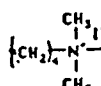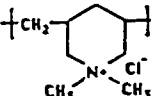| Polymer	Abbreviation	Structure
Poly(vinyl alcohol)	PVA	
Poly(acrylic acid)	PAA	
Poly(dimethylbutylammonium iodide)	PDBAI	
Poly(dimethyldiallylammonium chloride)	PDMDAAC	

Table 7. Elemental analyses of crystals grown from polymer solutions.

weight %	CONTROL	PVA	PAA	PDBAI	PDMDAAC
carbon	0.75	3.73	1.21	1.09	1.07
nitrogen	0.01	0.12	0.02	0.21	0.29
calcium	11.84	11.22	13.44	12.57	12.77
aluminium	14.65	13.87	17.73	15.5	15.60
iodine	---	---	---	1.68	---
chlorine	---	---	---	---	1.55
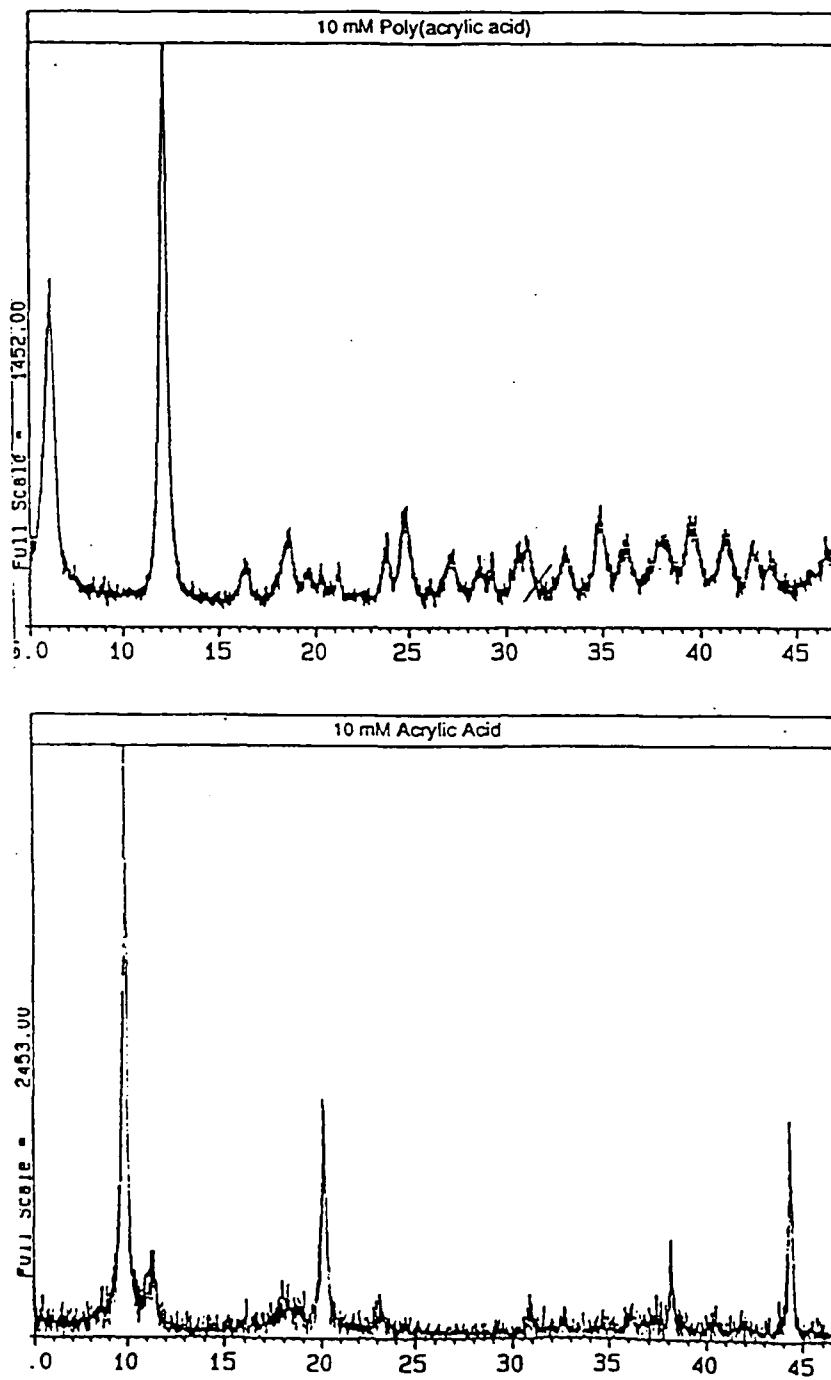
Figure 10. X-ray diffraction analysis of organoceramic powders formed in the presence of (a) poly(acrylic acid), (b) acrylic acid.

2.4 Cementitious Organoceramics

Objective: This project is investigating the synthesis of inorganic crystals in the presence of organic monomers or macromolecules with the objective of creating novel organoceramic structures that exhibit cementitious behavior. In addition to the specific goals of creating new materials the study may also provide insights on the mechanisms involved in polymer modification of cements.

Synthesis and Characterization: Various organoceramic powders have been synthesized from ionic solutions supersaturated with respect to aluminum and calcium-containing ions but dilute in concentration of organic molecules. These solutions are prepared from monocalcium aluminate and calcium oxide in distilled water. Various polyacids, polyols and polyelectrolytes were investigated this year and their structures are listed in Table 6. The organoceramic powders are precipitated at 2°C under a nitrogen atmosphere and then harvested after centrifugation. The results of elemental analysis of organoceramic powders are shown in Table 7. It is clear that all organoceramics have an increased carbon content indicating the presence of the polymer in the product; the I⁻ and Cl⁻ counterions in poly(dimethylbutylammonium iodide) (PDBAI) and poly-(dimethyldiallylammonium chloride) (PDMDAAC) were also detected by elemental analysis. At polymer concentrations less than 10 mM, x-ray diffraction scans of the organoceramic powders indicate that in all cases the main crystalline phase present is CAH_{10}. However, a very interesting result obtained recently is the observation that acrylic acid monomer leads to an entirely different crystalline phase (see figure 10). Over the next year we intend to learn more about the three dimensional structure of this hybrid material. Furthermore, a study of the impact of polymer concentration in the poly(acrylic acid) (PAA) system revealed the presence of different components as the concentration of polymer was raised. As shown in figure 11, intermediate concentrations of PAA lead to the formation of gibbsite and concentrated solutions result in the precipitation of an amorphous ionic network. These results suggest the possibility of using organic molecules to control the synthesis of inorganic phases.

Ultraviolet (UV) and fourier transform infrared (FTIR) spectroscopy were also used to characterize some of the organoceramics. Figure 12 shows UV spectra of the organoceramic powders recorded in diffuse reflectance. The polyelectrolyte PDBAI has a strong UV absorbance at 226 nm which can be seen in the diffuse reflectance spectrum of the PDBAI organoceramic. At the same time the PAA organoceramic also shows an increased absorbance at wavelengths less than 220 nm. This is most likely due to the

Glassy

Semi-Dilute
Polymer
Concentration

Gibbsite
Al₂O₃·3H₂O

Dilute Polymer
Concentration

CaOAl₂O₃·10H₂O

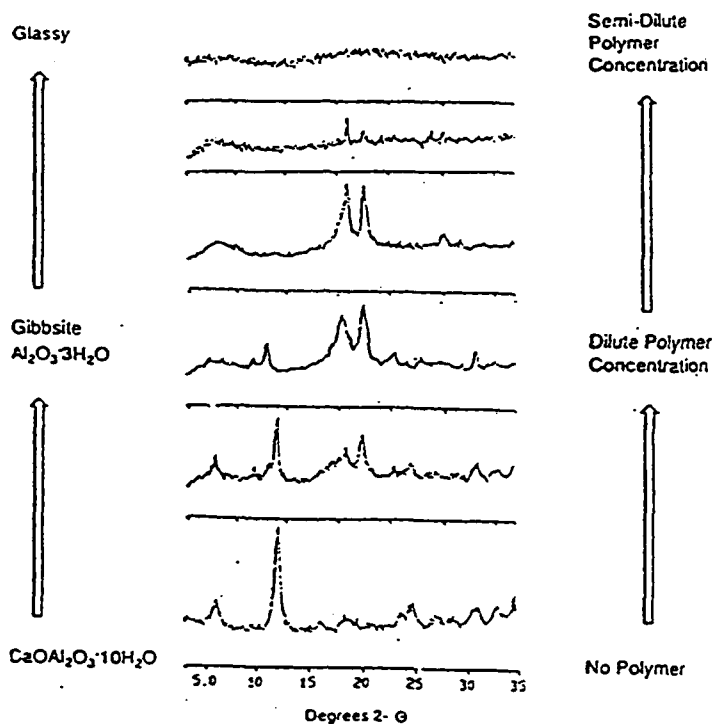No Polymer

5.0 10 15 20 25 30 35

Degrees 2- Θ

Figure 11.   Influence of PAA concentration on the composition and
crystallinity of organoceramic powders, as determined
by x-ray diffraction.

presence of the PAA, the latter having a UV absorbance centered at 214 nm. UV
characterization of the PVA and PDMDAAC is difficult since absorbance by these polymers
is small and easily disguised by that of the inorganic phase. FTIR spectra of KBr discs
containing the PAA organoceramic powder were obtained and Figure 13 shows the IR
spectra of the control powder (no polymer), the PAA organoceramic powder and a
difference spectrum obtained by subtraction of both spectra. The difference spectrum
clearly shows the existence of two bands at 1410 and 1570 cm⁻¹ corresponding to the
symmetric and asymmetric stretching of COO⁻ groups. The peaks indicate the presence of
metal carboxylate bonds in the organoceramic powder formed by ionization and
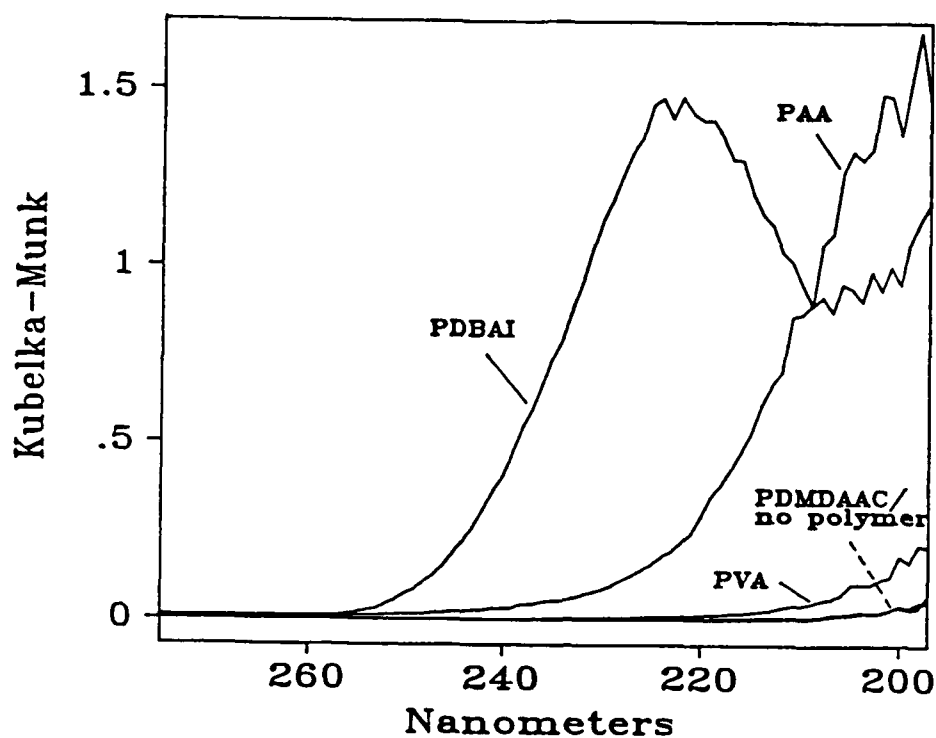complexation of PAA bonds with calcium or aluminum ions in the ceramic phase.

Figure 12. UV spectra of the organoceramic powders obtained by
diffuse reflectance (Kubelka-Munk units are linear with
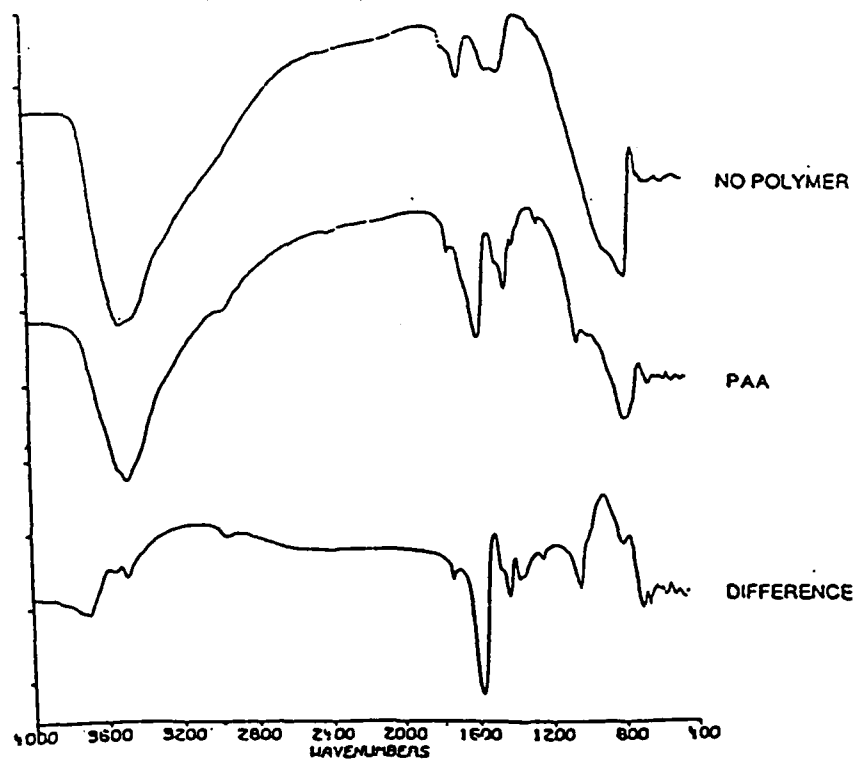concentration and are used in diffuse reflectance
spectroscopy).

Figure 13. FTIR spectra of the control (no polymer), PAA organoceramic
and their difference spectrum (PAA organoceramic-control).

Kinetics of Phase Transformations: The kinetics of phase transformation from the metastable CAH_{10} phase to other stable phases such as C_3AH_6 at increased temperature and humidity was followed using x-ray diffraction. Figure 14 shows transformation kinetics data for the control (no polymer) and the PVA organoceramic. In the absence of polymer the powder was found to be fully transformed within approximately 48 hours. However, the PVA organoceramic powder transformed at a much slower rate, with CAH_{10} still present after approximately 160 hours of aging. This transformation has often been associated with a decrease in strength of set pastes made form high alumina cement subjected to similar conditions. This is an interesting result in view of the fact that high strength macro-defect-free (MDF) cement formulations contain PVA as a polymer additive.

Microstructure and Mechanical Strength: We have initiated preliminary work on the structure and properties of "hybrid" cements containing organoceramic powders synthesized in our laboratory. We analyzed first by SEM the microstructure of set cements formulated with mixtures of a calcium aluminate cement (Secar 71) and 20% by weight PAA-organoceramic powder. Our micrographs indicate that the microstructure of hydrated
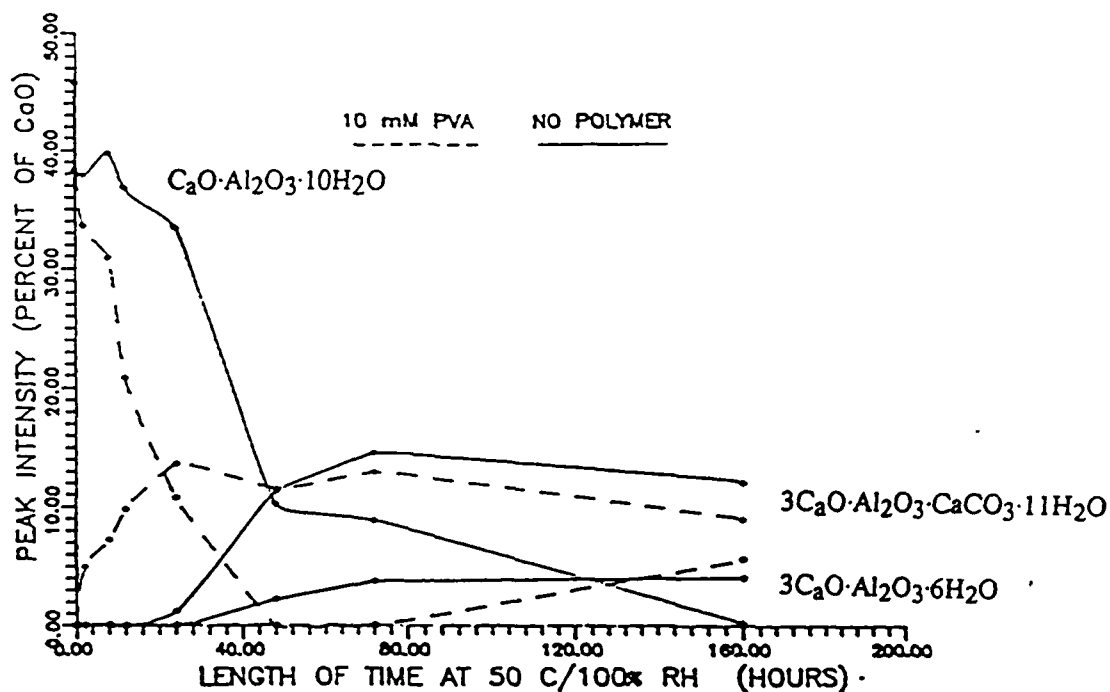
Figure 14. Transformation kinetics of organoceramic powders at 50°C and 100% R.H. Data points are taken from integrated peak intensities of x-ray diffraction scans of the partially transformed powders.

subjected to similar conditions. This is an interesting result in view of the fact that high strength macro-defect-free (MDF) cement formulations contain PVA as a polymer additive.

Microstructure and Mechanical Strength: We have initiated preliminary work on the structure and properties of "hybrid" cements containing organoceramic powders synthesized in our laboratory. We analyzed first by SEM the microstructure of set cements formulated with mixtures of a calcium aluminate cement (Secar 71) and 20% by weight PAA-organoceramic powder. Our micrographs indicate that the microstructure of hydrated Secar 71 at low temperature typically consists of grains of CA covered by a layer of hydration product. In the hybrid cement the layer of hydration products observed on CA particles of the calcium aluminate cement is not well defined. Also, the matrix between the particles of the hybrid cement seems more dense than the matrix of the Secar 71 cement. A preliminary study of mechanical behavior indicates that a 20% increase in compressive strength is achieved in the hybrid cements.

2.5   Polymer Interfaces

This project was cancelled in September 1988 due to lack of adequate staffing, despite some initially promising results. Efforts will be made to get the project reinstated at some future date.

2.6   Molecular Studies of Interfaces in MDF Cements

MDF cements have remarkably good mechanical properties compared to conventional cement pastes, but the origin of the mechanical strength is not clear. Also, problems with moisture sensitivity remain to be solved. Since interfacial regions in the composite are likely to play an important role in these characteristics study of the molecular aspects of interfaces has been underway. Three topics have been considered to provide a theoretical framework for future development.

1.   Polymer-Polymer Interfaces: These interfaces are very important in MDF materials due to internal weld lines formed during the rolling stage and also during other potential forming processes such as extrusion, lamination and injection molding of MDF materials. The underlying dynamics of the polymer chains controlling the structure development at the interface also has significant effect on the rheological properties.

3.   Percolation Effects: The structure of the MDF materials consists of an interpenetrating network of polymer in a network of cement. We are concerned with the nature of this network as a function of processing and composition. The interpenetrating PVA network occurs at the percolation threshold defined with respect to the volume percent of gelled PVA in the cement matrix and is considered to be a major cause of moisture sensitivity. This problem is being analyzed by computer simulation to determine the percolation effects and suggest processing solutions. The mechanism of transmission of mechanical forces through the randomly dispersed network structure and its effect on the fracture process is also unknown.

Polymer-Polymer Interfaces: The dynamics of interdiffusion of polymer chains at symmetric and asymmetric interfaces was analyzed. The concentration profiles $C(x,t)$ as a function of depth, x, time, t, temperature, T and molecular weight M, was calculated. Several time regions are examined involving: a) segmental motion, b) Rouse motion of entanglement segments, c) Rouse motion of the entire chain in a field of topological constraints, d) reptation and curvilinear motion of the whole chain across the interface, and e) long time Fickian Diffusion.

The molecular properties which can be measured experimentally were derived from the calculated concentration profile as follows. The total number of monomers crossing the interface, $N(t)$, behaves as:

$$N(t) \propto t^{3/4} M^{-7/4} \qquad (t < \tau)$$
$$N(t) \propto t^{1/2} M^{-1} \qquad (t > \tau)$$

where t is the time and M the molecular weight. The crossover in scaling laws at the repetation time τ is being explored by analysis of model deuterated/protonated polymer interfaces by SIMS and Neutron Reflectivity (NR) at Argonne National labs. The NR experiments are done using the Intense Pulsed Neutron Source (IPNS) at low grazing angles such that total reflection is obtained at low neutron momentum. Initial results form the SIMS and NR experiments are highly supportive of the Zhang-Wool theory of polymer-polymer interfaces.

Interestingly, the modified single chain repetation dynamics approach used to give a good description of the interface structure was not found to be correct for describing the melt viscosity of polymers. This was observed from infrared dichroism relaxation studies of centrally deutrated chains. The resolution to this problem is believed to lie with the

network relaxation versus the single chain relaxation mechanism currently used to describe viscosity in polymer melts. This problem will be examined by determining the vector percolation aspects of network relaxation such that entanglements are broken by single chain dynamics, but the mechanical response is determined by percolation of forces through the randomly connected network. Initial studies with model networks on a tensile tester provide excellent initial support to this concept.

The information gained form the studies on polymer-polymer interfaces will be used in the design of model mechanical experiments on interfaces, processing histories and material selection.

Polymer-Cement Interfaces: The fractal characteristics of the interdiffusion of metal ions into a polymer substrate was analyzed by computer simulation. The diffusion field could be divided into two sections. A connected region interface zone near the cement substrate was separated from the interphase region in the polymer substrate by a diffusion front such that the metal ions were encapsulated in the polymer matrix. The diffusion front was found to be highly ramified and the roughness of length of the front, L_f, could be described by:

$$L_f \propto X^{(1-1/D)}$$

where X is the average interpenetration distance and D is the fractal dimension. The fractal characteristics are found to be generic to all interdiffusing species and the local microstructure is uniquely described by this model. The results of this work are being applied to SIMS analysis of model interfaces and to provide a framework for relating chemical reactions and structure to the strength of polymer-cement interfaces.

Percolation Effects: The optimum composition of PVA in cement is found to be that which provides a continuous network of PVA in the cement matrix. This is highly advantageous from a processing viewpoint but has serious consequences for the resulting moisture sensitivity and mechanical properties of the finished MDF material. A computer simulation study of the percolation process for finite sized plates was conducted as a function of the volume percent PVA gel. It was found that the threshold occurred at $p_c = 0.31$.

The consequences for MDF materials with regard to percolation phenomenon are as follows. The volume percent of PVA gel is determined with respect to both the PVA and water content. Correcting for density in the optimal ICI formulation, we see that the gel is above the percolation threshold. When the material is formed, the PVA has a continuous network in the cement matrix which can "conduct" water through the material. Since the threshold is quite sharp, the processing mix can be redesigned with non water conducting

additives which facilitate the processing rheology but permit the MDF material to exist below the PVA percolation threshold. Below, p_c, the limited penetration of water into the matrix is being explored as a potential toughening mechanism. The results on percolation effects are being used to design processing experiments where the final PVA content will be below the threshold for predicted water sensitivity.

2.7 Magnesium Phosphate Cements

The objective of this project is the preparation and characterization of magnesium polyphosphate cements and comparison of their properties with analogous monophosphate cements in order to determine the influence of polyphosphate chain length on the chemical and physical properties of the cement paste. During the past two years, magnesium ammonium triphosphate cements have been prepared for the first time and demonstrated to have radically different properties than magnesium ammonium monophosphate cements. The research has set the stage for the development of long-chain polyphosphate cements whose properties might be manipulated by varying chain length and degree of crosslinking, thus applying traditional polymer processing techniques to ceramic processing.

Processing: Rapid-setting phosphate cement pastes are prepared by hydration of MgO plus $(NH_4)_2$-HPO_4 according to the equation:

$$MgO + (NH_4)_2HPO_4 \xrightarrow{\quad H_2O \quad} Mg(NH_4)PO_4 \cdot 6H_2O + NH_4OH \qquad (1)$$

Numerous investigations have established magnesium ammonium phosphate hexahydrate (struvite) as the reaction product using X-ray powder diffraction techniques.

By analogy with the above equation, triphosphate cements have been prepared by hydration of MgO plus $(NH_4)_3H_2P_3O_{10}$. Although a cementitious material is prepared, it has properties very different from the monophosphate material. In the monophosphate case, the paste sets within a few minutes to a rigid body and strength is fully developed within about 15 hours. In the triphosphate case, the paste also sets within a few minutes, but to a readily deformed material that slowly becomes rigid over the course of about 24 hours, and develops full strength only after about 8 days.

Structural Characterization: The monophosphate cement described above yields struvite as the sole crystalline hydration product, and the course of the reaction can be

monitored by X-ray powder diffraction. In contrast, the triphosphate system yields only an amorphous material upon hydration, and X-ray powder dif-fraction is therefore incapable of identifying the reaction products.

Examination of the monophosphate system by ^{31}P MAS NMR showed struvite as the only hydration product. Examination of the hardened triphosphate cement paste indicated both monophosphate (<5%) and triphosphate (>95%) species are present as hydration products. Triphosphate was readily identified by resonances at -7 ppm and -18 ppm for phosphorus nuclei at the ends and center of the $P_3O_{10}^{5-}$ chain, respectively (see Figure 15). These resonances are readily distinguishable from resonances for $(NH_4)_3H_2P_3O_{10}$ that appear at -10 ppm (terminal P) and -22 ppm (central P).

Compressive Strength: Stress/strain curves for monophosphate and triphosphate cements are shown in Figure 16. The monophosphate cement compressive strength of 3200 psi agrees well with literature values. The 9000 psi compressive strength measured for triphosphate cement is obtained from samples poured into cylindrical molds without applying external pressure. Application of manual pressure to the sample during early stages of curing leads to compressive strengths of over 15,000 psi.

Porosity: Mercury intrusion porosimetry was used to determine pore volumes and pore size distributions in monophosphate and triphosphate cements (see Figure 17). A bulk density of 1.9 g/mL and a skeletal density of 2.7 g/mL were observed for the monophosphate case; corresponding values of 2.5 and 2.7 g/mL were obtained for the triphosphate system. The higher strength of the triphosphate cement is thus easily accounted for in terms of lower porosity.

2.8 Microstructure of DSP Pastes

Studies during this past year have concentrated on the the pore structure of hardened paste and the chemistry of hydration under autoclaving conditions.
Pore structure: Previous work indicated that the porosity of hydrated DSP pastes is largely confined to microporosity associated with the C-S-H matrix. An extensive analysis using the full nitrogen adsorption isotherm has shown that even micropore volumes are quite small for DSP pastes compared to pastes made only with cement, but with a
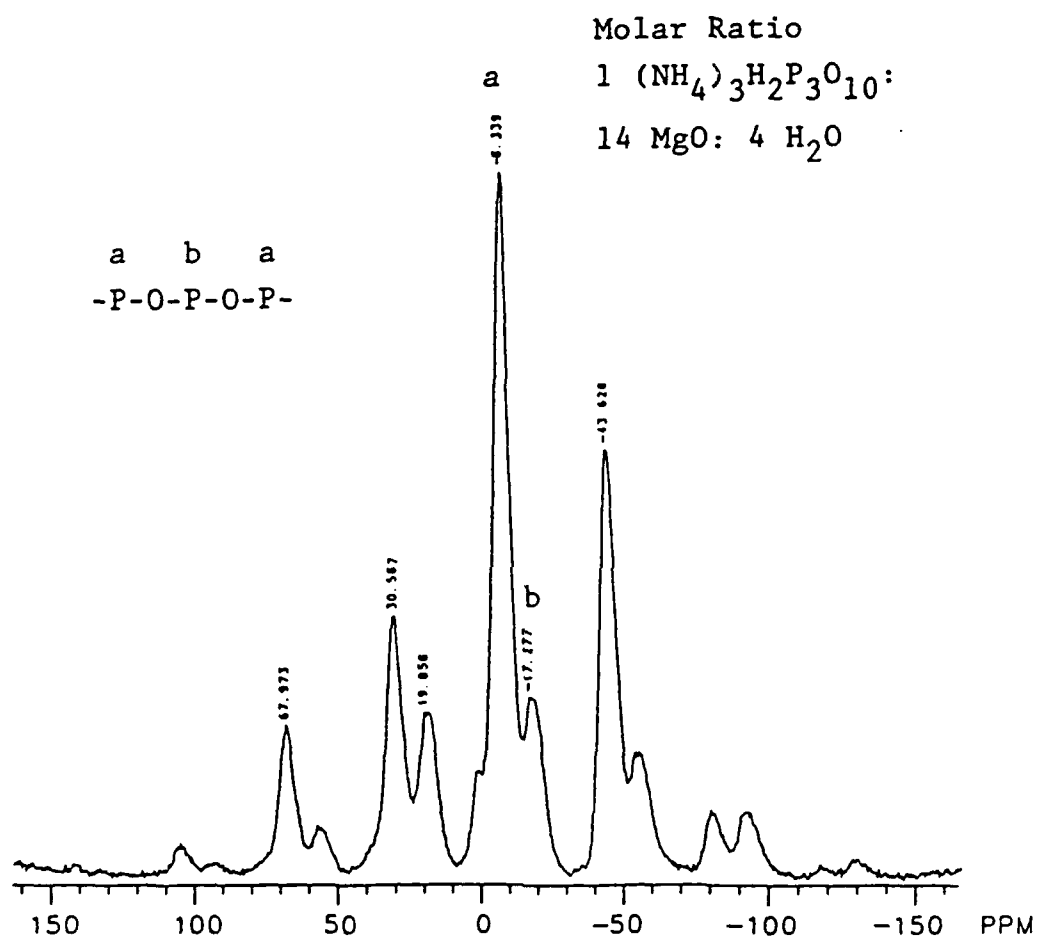
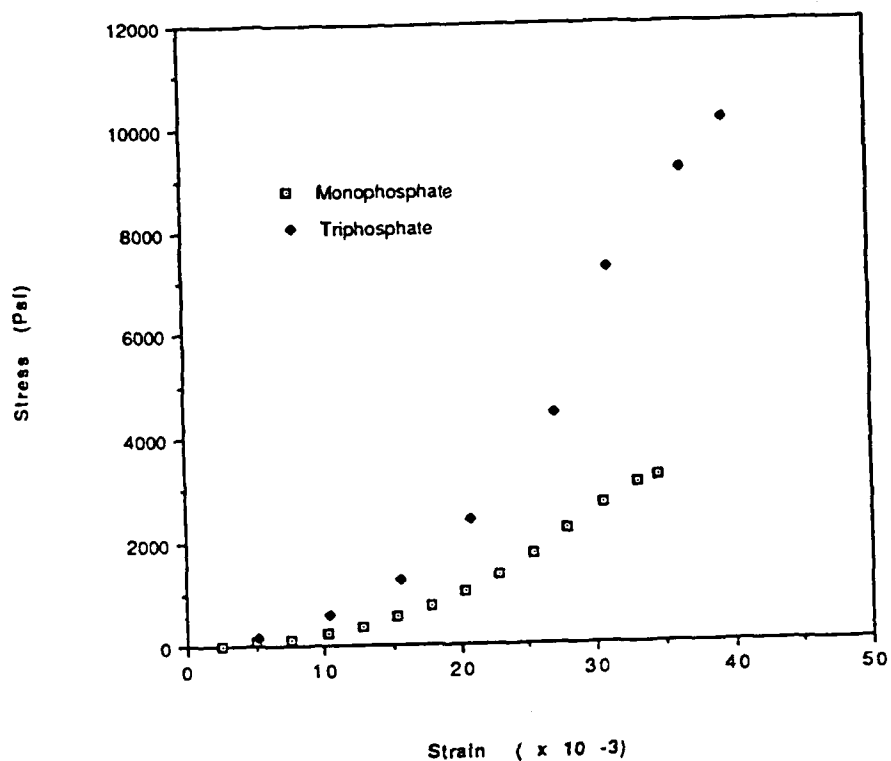Figure 15. ^{31}P MASNMR spectrum of the reacted MgO-$(NH_4)H_2P_3O_{10}$-H_2O system.

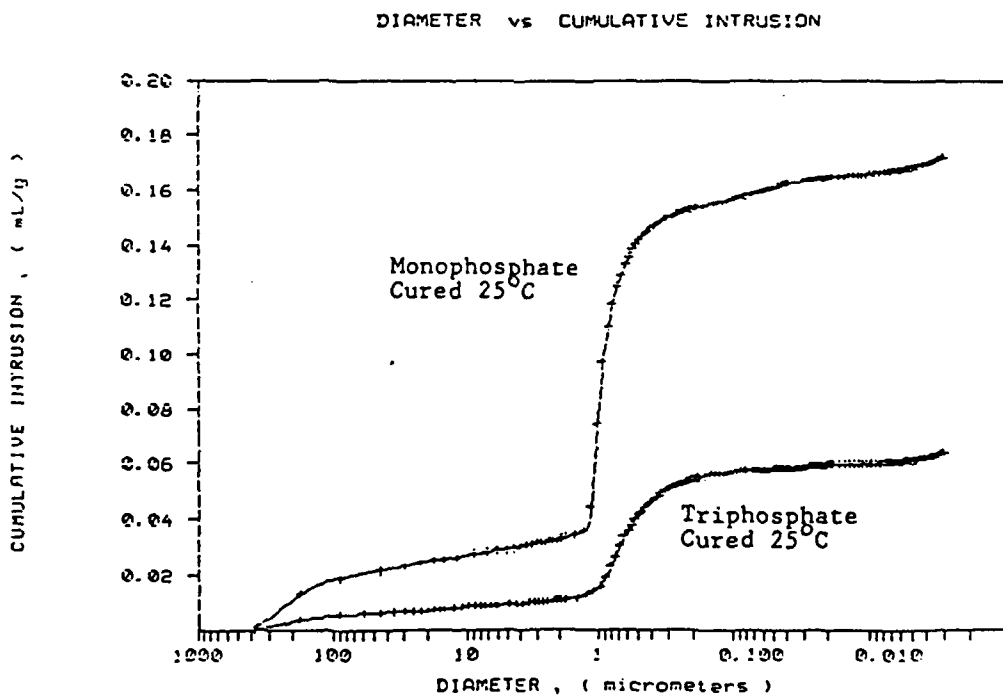Figure 16. Stress-strain curves for magnesium monophosphate and triphosphate cements.

Figure 17. Mercury intrusion porosimetry curves for magnesium manophosphate and triphosphate cements.

comparable water:cement ratio. The comparison is shown in Figure 18, where the data is presented as V-t plots. The slope of the initial linear segment is proportional to the surface area, while downward deviations from this line represent filling of micropores and upward deviations represent capillary condensation in mesopores. It can be seen that all the pastes have only micro-porosity, but when silica fume is present the volume of micropores (i.e. the magnitude of the downward deviation) is much less. This is thought to be due to the fact that there are pores present that are too small to be penetrated by the nitrogen molecule. This has been confirmed by the measurement of the water adsorption isotherm. Surface areas approaching 200 m^2/g paste are measured by water vapor adsorption.

It has previously been shown that the pore structure depends on the way the pastes are dried before adsorption measurements. This is known to be true for conventional cement pastes, but has been found to be even more critical for DSP pastes. It appears that internal stresses developed during drying result in pore collapse and the conversion of some microporosity into mesoporosity. An extensive study of the phenomena has been carried out and the results shown in Figure 19. Methanol replacement followed by vacuum evaporation of the methanol has been the routine method of drying. However, figure 19 shows that it would be better to remove the methanol by critical point drying. Since this avoids the formation of a liquid meniscus and the concomitant surface tension forces, it should be the least disruptive of all methods used. Surface area measurements confirm this assumption, although the highest value is still less than that obtained by water adsorption. At present we are not in a position to be able to use critical point drying on a routine basis. The use of the current drying stratagem is the best alternative. The information obtained in this study is now being applied to modelling how the adsorption of water vapor affects the electrical properties of DSP pastes.

Hydration Chemistry: Previous work has shown that space limitations control the extent of cement hydration in DSP pastes. Quantitative measurements using the trimethylsilylation (TMS) derivatization method suggests the limit for hydration is about 30-35%, which agrees quite well with the value calculated using a typical reaction stoichiometry for cement-pozzolan reactions. It would, however, be desirable to determine reaction stoichiometries directly to see if there are significant changes in the C-S-H composition in various DSP formulations (up to 36% silica fume). Both TMS and 29-Si MAS NMR spectroscopy studies show an increase in the degree of silicate polymerization, and the presence of a cyclic trimer (see figure 20a), which has not been reported previously. NMR spectroscopy reveals the presence of unreacted silica fume (Figure 20b), and efforts are now underway to quantitatively determine amount of unreacted silica fume.
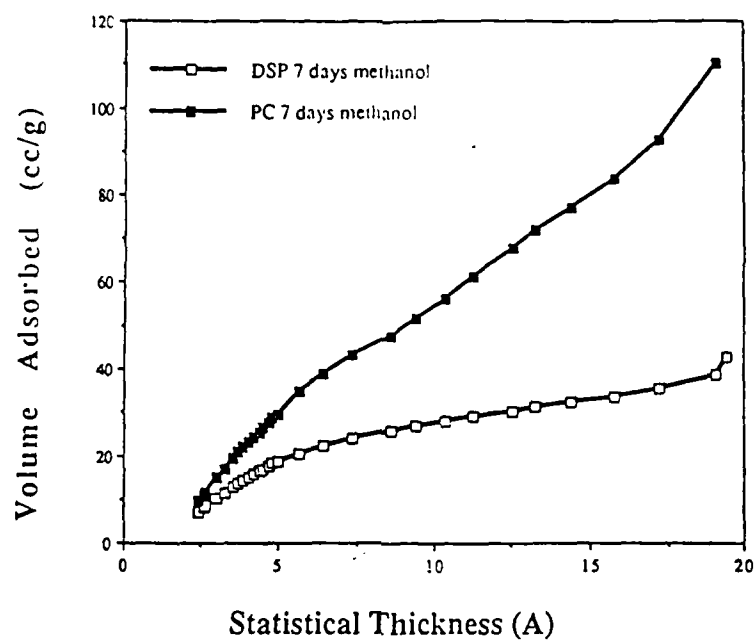
Figure 18.   V-t plots constructed from nitrogen adsorption data for conventional cement paste and DSP cement paste. (Dried by methanol replacement).
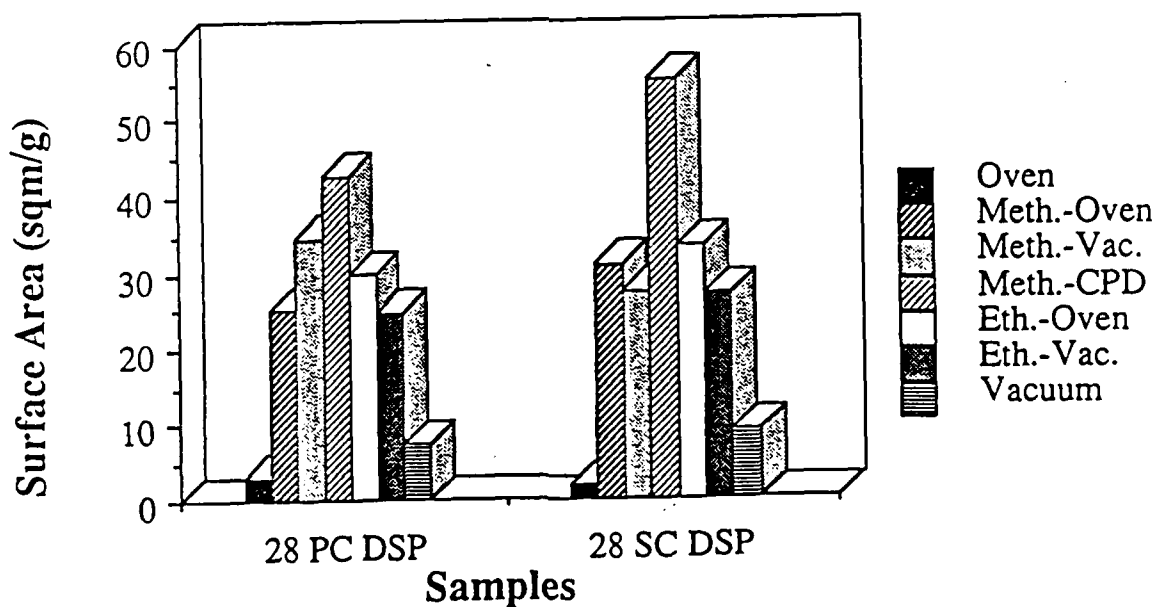

Figure 19. Effect of different drying methods on surface area of 28-day old DSP cement pastes.   PC = portland cement; SC = slag-portland cement blend.

The amount of calcium hydroxide is being measured quantitatively using X-ray diffraction and thermogravimetric analyses. ~~29-Si MAS NMR is being used to determine the~~ A major problem has been to find a suitable internal standard that will allow an accurate determination, since the composition of C-S-H is determined by difference. Quantitative results of acceptable accuracy are expected soon.

An extensive examination of the autoclaving of DSP formulations has been undertaken using 29-Si MAS NMR and x-ray diffraction. The results are summarized in Table 8. The most interesting observations that emerge from this study are:

1. C-S-H formed at elevated temperatures does not show any signs of crosslinking (there are no Q_3 species present), but the Q_2/Q_1 ratio increases with increasing temperature and decreasing C/S ratio (see Table 9).

2. At 183 C almost all the cement is hydrated by 36 hr.

3. Kilchoanite and related $8CaO.5SiO_2$ are formed at 240°C. Both appear to contain structural water.

2.9   Setting Processes in Cementitious Systems

The strength and durability of materials derived from suspensions (e.g. cement pastes) are typically limited by porosity. Decreases in porosity are usually achieved by increasing the solid's packing fraction. In the case of cementitious systems, this is accomplished by controlling the cement grain size distribution or loading a cement with small particles that act to fill pores left by the larger cement grains (i.e. DSP cements). However, the fraction of the suspension volume occupied by particles can be raised only so far before the suspension is no longer flowable and thus stops being useful as a castable material. Thus questions arise about the limits of solid's loading and the best ways to achieve flowable suspensions which result in low porosity solids.

For a typical cement, the problem of controlling porosity is not just limited to how cement grains pack. Chemical reactions resulting in setting play a key role in determining pore size distribution. Pores are generally locked into place during the initial stages of the setting reaction where the cements grains become bonded together. Understanding packing fraction limitations on the flowability of suspensions, and developing tools for characterizing the development of rigid structures in setting cements is the thrust of this work.

The rheological properties of suspensions are determined by particle interactions averaged over the suspension structure. As a result, a single flow parameter such as viscosity or elasticity is unable to provide a unique characterization of both interaction and

structure. The initial stages of this project have concentrated on developing the tools that can be used to extract both structural and interaction potential information from the flow properties of dense suspensions.

Model Systems: For these preliminary studies model suspensions were used where the particle interactions and suspension structures could be varied in a known manner. Suspensions of gelled, uniformly sized, spherical particles were used for this work. Gelation was accomplished by increasing particle volume fraction to values between 0.48 and 0.62. For the systems being studied, particles interact with purely repulsive pair interactions. As the volume fraction in a suspension is raised, an order/disorder transition is observed above which the suspension behaves like a gel in that it is elastic and has a yield stress and thus acts like a model system for a setting cement. The phase transition which brings about this gelation is one where the particles order into a well defined lattice as indicated by the colorful iridescence of the gelled suspensions that is brought about by Bragg diffraction off particle layers spaced on the order of the wave length of visible light.

Rheological Behavior: The creep and recovery behavior of suspensions gelled in this manner were measured as a function of the strength of the pair interactions, and solid's volume fraction using a Bohlin Constant stress Rehometer purchased by the Center. In these experiments a suspension is loaded into the rheometer, sheared at a high rate of deformation, and allowed to recover for a long period of time (>3 hrs). Subsequently, a constant stress is applied to the suspension and its deformation measured as a function of time. After a predetermined time, the stress is released and the recovery of the suspension is followed. For an elastic solid, the strain on application of the stress shows a jump to a steady state value, whereas for a Newtonian liquid the strain increases linearly with time. When the stress is released, the elastic solid will show complete strain recovery, while the Newtonian liquid shows no recovery at all. Depending on the magnitude of the stress applied, the gelled suspensions studied here displayed solid-like, Newtonian liquid-like, or a combination (viscoelastic) of these behaviors.

All of the gelled suspensions investigated showed four types of behavior upon application of the stress. At low stresses the suspensions behaved like elastic solids with elastic moduli that were functions of pair interaction energy and increased exponentially with volume fraction. At larger stresses the suspensions deformed in a very sluggish manner not reaching a steady state rate of deformation even 3.5 hrs after application of the stress, and complete strain recovery was not observed. At still larger stresses, over a very narrow stress range, the suspensions suddenly showed viscoelastic flow behavior in that steady state rates of deformation were reached in times shorter than 500 s and a well-

defined viscosity could be defined. The stress where this change in flow behavior occurs corresponds to a dynamic yield stress that is also a funtion of particle interaction potential and increased exponentially with volume fraction. At stresses above the yield stress, the suspensions showed a viscosity that decreases with increasing shear rate. However, at a critical shear rate, which was again a function of pair interaction energy and increased exponentially with volume fraction, the viscosity dropped 1-3 orders of magnitude in a discontinuous manner. For higher stresses, the suspension viscosity appeared to decrease to a Newtonian high stress plateau value.

In addition to viscosity data, the recoverable strain was observed to undergo dramatic changes as the stress was increased. At low stresses the recoverable strain equalled the strain on application of the stress and increased linearly with stress. At higher stresses the recoverable strain increased approximately with the cube of stress and at the yield stress there was a sudden break in the slope of the recoverable strain/stress plot. At higher stresses the recoverable strain increased to a maximum value and then decreased sharply; the maximum value occurring at the critical stress where discontinuous shear thinning occurred. Remarkably, the recoverable strain at the yield stress was independent of pair interaction potential and volume fraction, giving a value of 0.04. The same was true of the recoverable strain at the critical stress where the average value was 0.06. Indeed, if the stress were scaled on the equilibrium modulus of the suspension (as measured at low stress levels) the recoverable strain curves for a wide range of volume fractions superimpose. **Microstructural Interpretation:** These results can be understood in terms of the suspension microstructure. In all of the gel suspensions the particles are arranged in a crystalline lattice. The lattice type is insensitive to volume fraction or particle interaction potential (over the range of potentials investigated here). As a result, all of the suspension structures were essentially the same with only the nearest neighbor spacing and magnitude of the pair interactions varying. The experimental results indicate that the pair interactions determine the magnitudes of the elasticity of the equilibrium structure, the yield stress and the critical stress. However, the time average deformations where critical events occur in suspension deformation depend only on suspension microstructure which is invariant in the wide range of systems studied. As a result, these studies suggest that while the magnitude of the stress required to strain the equilibrium structure a given amount depends on the details of the interaction potentials, the strains where critical events occur are functions solely of packing geometry. The structural rearrangements occuring at the yield stress that allow flow to occur and at the critical stress where the dramatic reduction in viscosity is observed are under study with neutron scattering experiments currently under development.
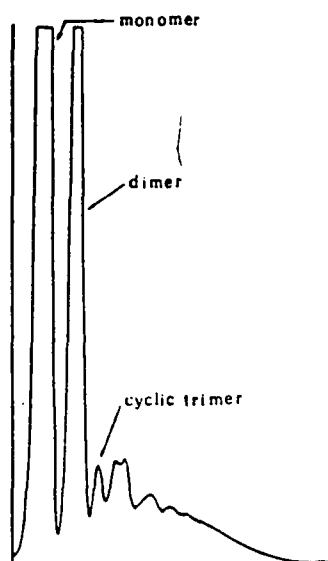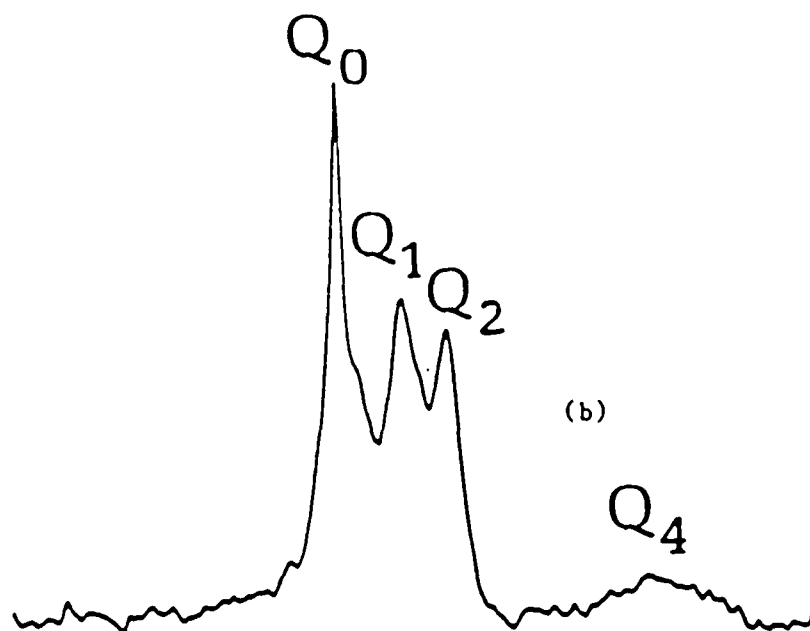
Figure 20.   Analysis of silicate polymerization in a DSP cement
paste (24 wt% silica fume, hydrated 6 mo.) (a) TMS
chromatogram (b) ^{29}Si MAS NMR spectrum.

Table 8   **Hydration Products of DSP Cement Formulations at Elevated Temperatures (36 hours reaction)**

Temperature °C	CaO/SiO$_2$ Molar Ratio			
	1.4	1.3	1.1	0.8
65	C-S-H CH	C-S-H (CH)*	C-S-H	C-S-H
120	C-S-H CH	C-S-H (CH)	C-S-H	C-S-H (Tobermorite)
183	C-S-H (CH)	C-S-H	C-S-H (Tobermorite) (Xonotlite)	Tobermorite (C-S-H)
240	Kilchoanite C$_8$S$_5$	Kilchoanite (C$_8$S$_5$)	Xonotlite (Scawtite)	Tobermorite (Xonotlite) (Scawtite)

#C = CaO, S= SiO$_2$, H = H$_2$O; + 1.13 nm variety
*( ) denotes phases present in minor cements;

Table 9   **Changes in Silicate Polymerization of C-S-H Formed at Elevated Temperatures**

Temp./Time	CaO/SiO$_2$ Molar Ratio			
	1.4	1.3	1.1	0.8
65°C/36 hr	0.33	--	--	--
120°C/36 hr	0.40	0.90	1.22	2.17
183°C/18 hr	0.58	--	--	--
183°C/36 hr	0.75	--	--	--
183°C/72 hr	1.13	--	--	--
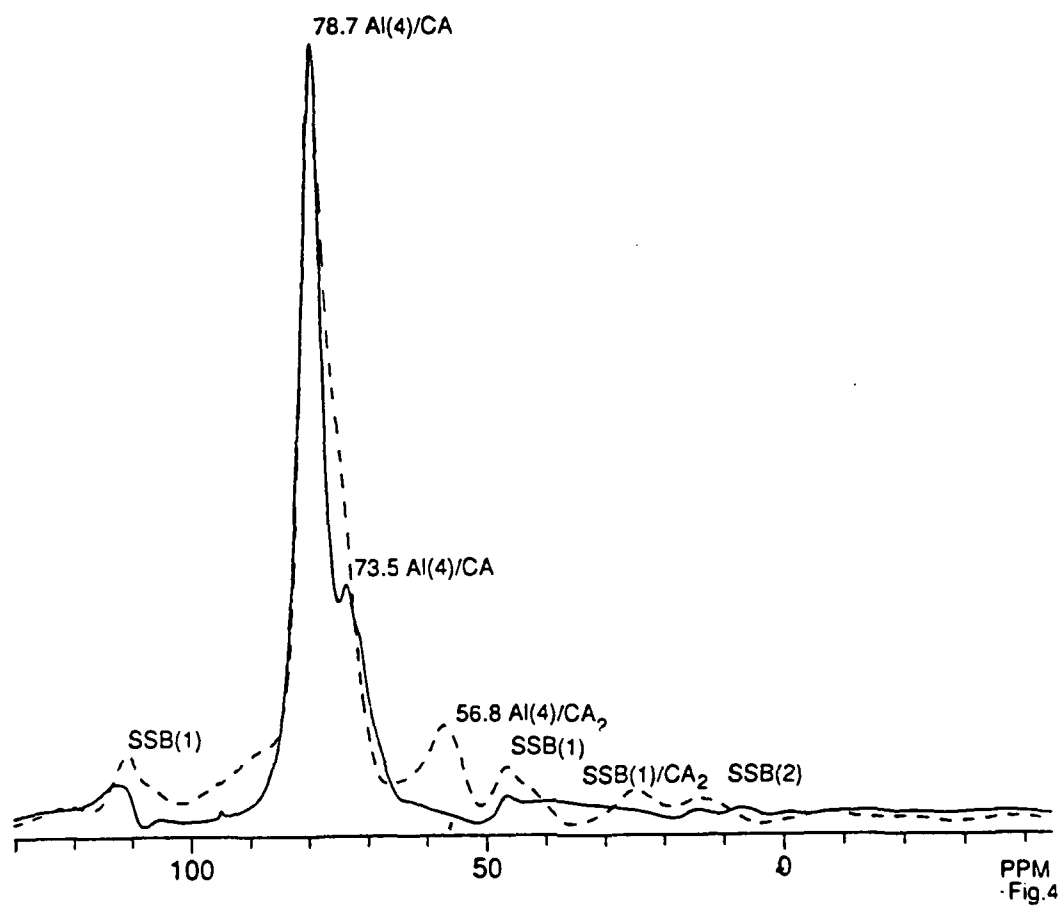
Figure 21. ^{27}Al MAS NMR spectra (a) calcium aluminate cement
(full line); (b) CaO·Al$_2$O$_3$ (dashed line).

In essence, these studies suggest that recoverable strains can be used to characterize suspension structure and, that equilibrium moduli can be used to characterize the strength of pair developed for systems with well defined particle packings and purely repulsive pair interactions. The next step is to determine if these scaling relationships hold for more complex gelled suspensions. Currently dense, flocculated suspensions (i.e., where pair interactions are attractive) and Portland cements are under study. Preliminary studies suggest that the scaling relationships continue to hold.

2.10 High-Resolution NMR Spectroscopy of MDF Cement Systems

During the last year the main emphasis of this work has been the study of the hydration reactions of calcium-aluminate-based MDF cement, particularly Secar 71, using high-resolution solid-state ^{27}Al nuclear magnetic resonance (NMR) spectroscopy. In addition, we have provided consulting for other members of the Center on NMR methods and have run samples for them using our high-field NMR spectrometers. The latter work is described elsewhere in this report.

^{27}Al NMR is an excellent method to study reactions in Ca-aluminate based cement systems. It readily detects changes in the local Al structural environment (tetrahedral Al [Al(4)] and octahedral Al [Al(6)] are easily resolved). In addition, the proton-cross-polarization (CP) method enhances the signal for Al in the hydration products and suppresses the signal for Al in the anhydrous reactants, providing a clear separation of signal for the products and reactants. All the NMR spectra were obtained at a magnetic field of 11.7T (500 MHz proton frequency) under magic-angle spinning (MAS) or proton-cross-polarization MAS (CPMAS) conditions. Most samples were also examined by powder x-ray diffraction (XRD).

Experiments with Calcium Aluminate Cement: Secar 71 is a commercially available cement, used in MDF cements, which is composed of $CaO \cdot Al_2O_3$ (CA) and $CaO \cdot 2Al_2O_3$ (CA_2), with CA being the major reactant. The 27-Al MAS NMR spectrum (Figure 21) shows that only Al(4) species are present. When reacted with water the NMR spectra shows the elimination of CA and the development of signals near 10 ppm , which correspond to Al(6) species, as seen in Figure 22. The CPMAS spectra confirm that these signals belong to hydrated species. At 80 C the presence of C_3AH_6 and crystalline $Al(OH)_3$ is confirmed by x-ray diffraction (see Table 10). At 6°C a similar peak is seen, but it is broader. X-ray diffraction shows CAH_{10} is formed, but amorphous products may also

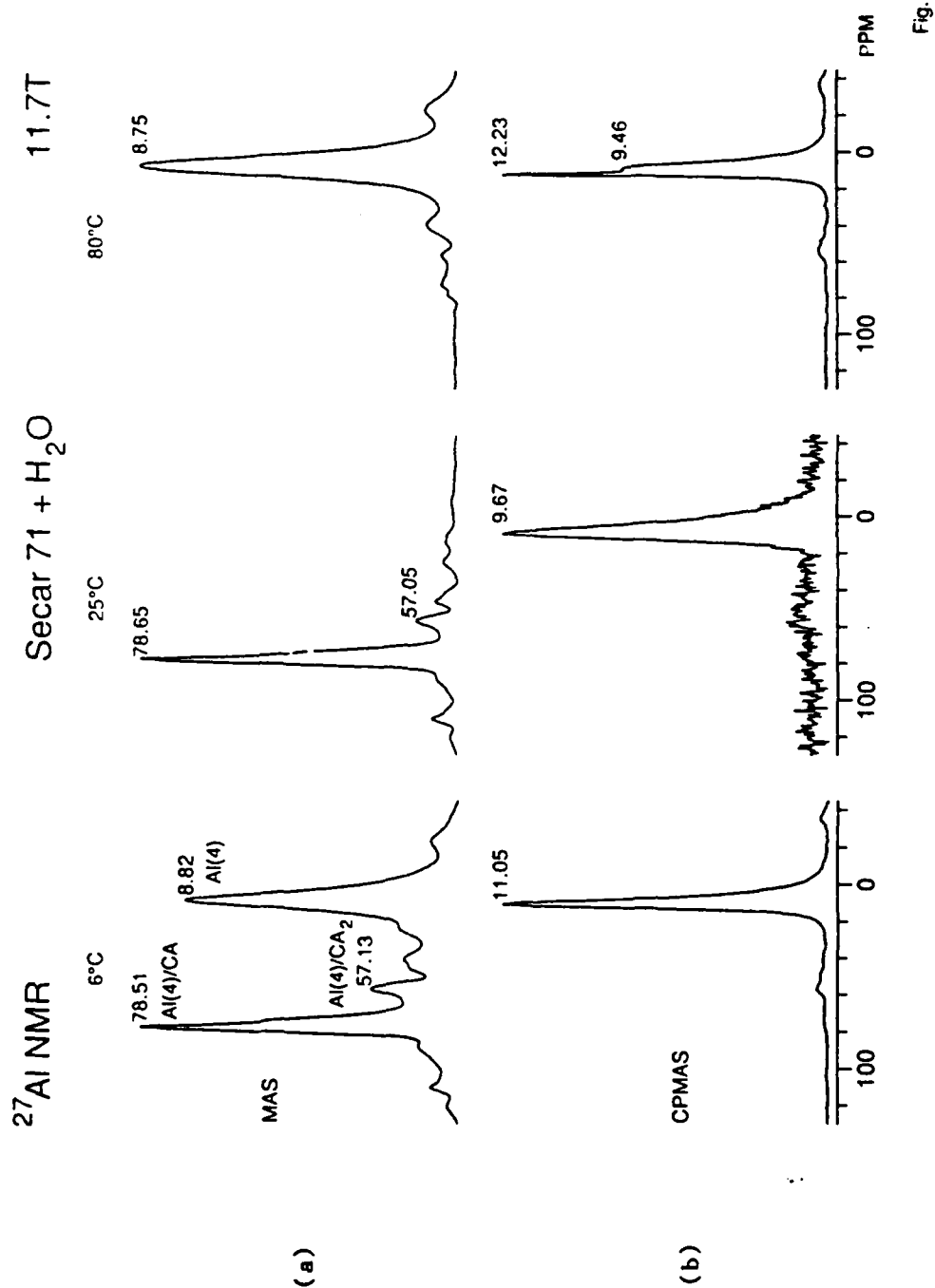Figure 22. ^{27}Al NMR spectra of hydrating calcium aluminate cement at different temperatures (a) MAS spectra (b) CPMAS spectra.

occur, as is the case at 25°C. The rate of hydration at 25° was the least of the three studied; the reasons for this anamolous result, are not understood.

When polyvinyl alcohol (PVA) is added, XRD shows no crystalline products at 25 and 6°C, but NMR spectra confirm that similar reactions are occurring. The relatively large width of the Al(6) peaks in samples where no products are observed by x-ray diffraction indicates that the products are amorphous. PVA appears to retard the rate of reaction and degrade the crystallinity of the products.

Table 10. Hydration Products of CA Identified by X-ray Diffraction

CA origin	Addition	6°C	25°C	80°C
In cement	--	CAH_{10}	--	C_3AH_6 $\alpha-\&\beta-Al(OH)_3$
Synthetic	--	CAH_{10}	CAH_{10} $\alpha-Al(OH)_3$ C_2AH_8 C_4AH_x	C_3AH_6 $\alpha-\&\beta-Al(OH)_3$
In cement	+5% PVA	--	--	C_3AH_6 $\alpha-\&\beta-Al(OH)_3$
Synthetic	+5% PVA	C_2AH_8 CAH_{10}	C_2AH_8 $\alpha-Al(OH)_3$	C_2AH_8 $\alpha-\&\beta-Al(OH)_3$ C_3AH_6
In cement	+10% PVA	--	--	C_3AH_6 $\alpha-\&\beta-Al(OH)_3$
Synthetic	+10% PVA	CAH_{10}	C_2AH_8 $\alpha-Al(OH)_3$	C_2AH_8 $\alpha-\&\beta-Al(OH)_3$ C_3AH_6

Experiments with CA: The presence of CA$_2$ in Secar 71 complicated interpretation of the NMR spectra, because signal form its Al-site is broadened by second-order quadrupole effects. Thus, some experiments were also carried out with pure CA in order to remove the interference from unreacted CA$_2$. The results are essentially the same as for the cement, but the crystallinity of the products is better at the lower hydration temperatures, as seen in Table 10.

Insitu kinetic experiments: To better understand the kinetics of the hydration reactions and the effect of PVA on the reaction rate, and to test the feasibility of using in situ experiments in the spectrometer in combination with CPMAS to quantitatively measure reaction rates, experiments were carried out with Secar 71 + water and Secar 71 + water + 5% PVA. To our knowledge, these are the first such experiments ever undertaken. Their success shows that this kind of experiment has great potential in investigating cement reactions. The runs were performed at room temperature by placing the reactants in an O-ring sealed MAS NMR rotor, rapidly starting the NMR experiment, and collecting CPMAS spectra at 30 minute intervals. The intensity of the CPMAS signal from the product phases is used as a measure of the extent of reaction.

The results (Figure 23a) show that the reaction extent follows the classic sigmoidal form of nucleation and growth controlled reactions and that the presence of PVA greatly retards the reaction rate. The run with PVA present was not carried to completion due to limited spectrometer time.

The classical expression for the extent of a nucleation and growth controlled reaction is

$$\phi = 1 - \exp\left(-\frac{\pi}{3} I Y^n t^{n+1}\right)$$

where ϕ is the relative volume of the products, I and Y are the nucleation and growth rates respectively (both assumed constant), n is the average dimensionality of the product grains, and t is reaction time. The value of n can be determined form plots of the form shown in Figure 23b. The linear relationships in Figure 23 show that these reactions are well described by this theory. The value of n is about 4.6 for the reaction without PVA which indicates a 3-dimensional shape for the product grains and an increasing rate of nucleation and/or growth. When PVA is present n drops to, which indicates a 1-dimensional shape for the product grains and constant rates of nucleation and growth.

Results for MDF Cement: The NMR results for a series of heated and hardened MDF cement based on Secar 71 and PVA with and without small amounts (<< 1%) of added Si and B (Figure 24) show that the added components have no detectable effect on the
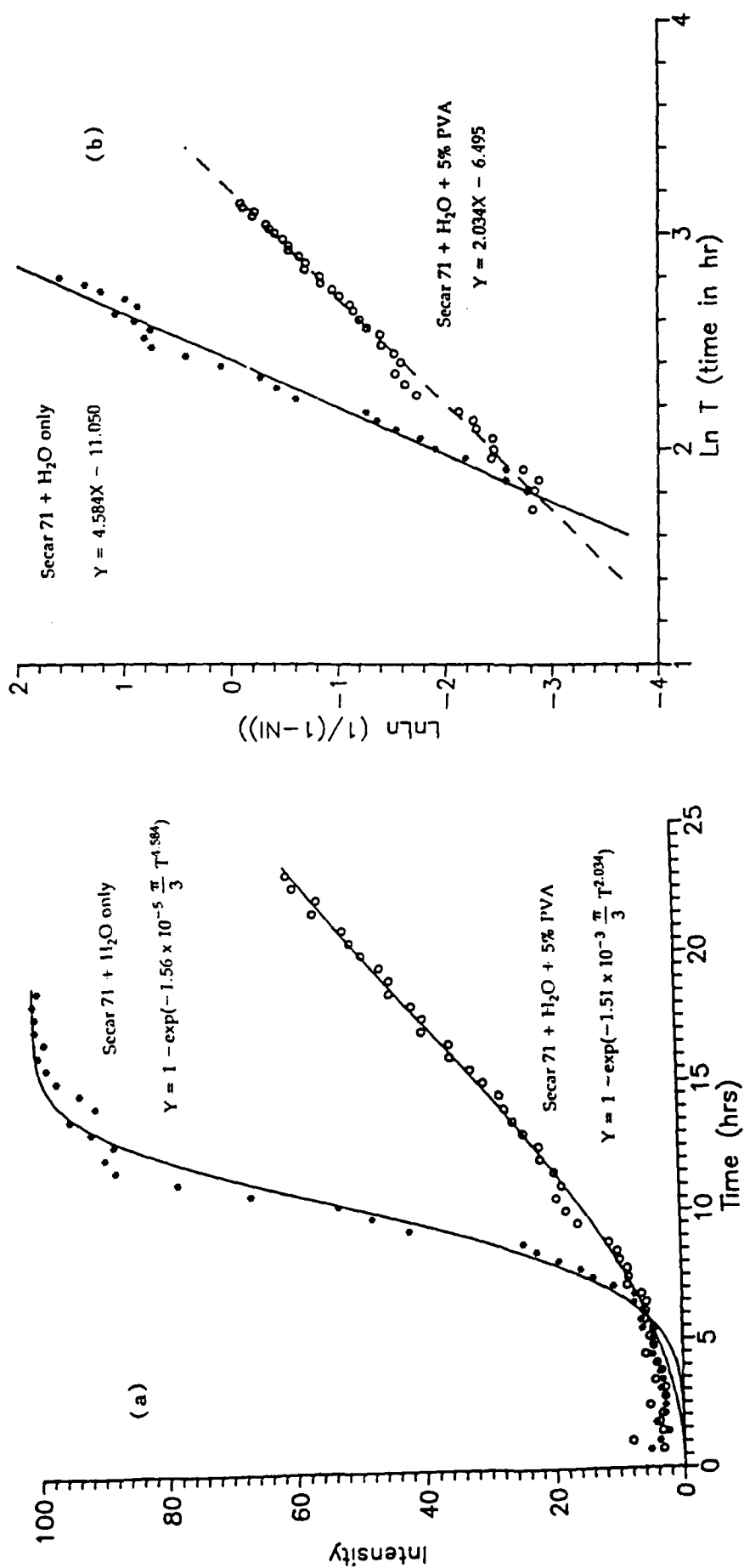
Figure 23. Kinetic data for hydration of calcium aluminate cement (Secar 71), with and without PVA, as determined by ^{27}Al CPMAS NMR studies.
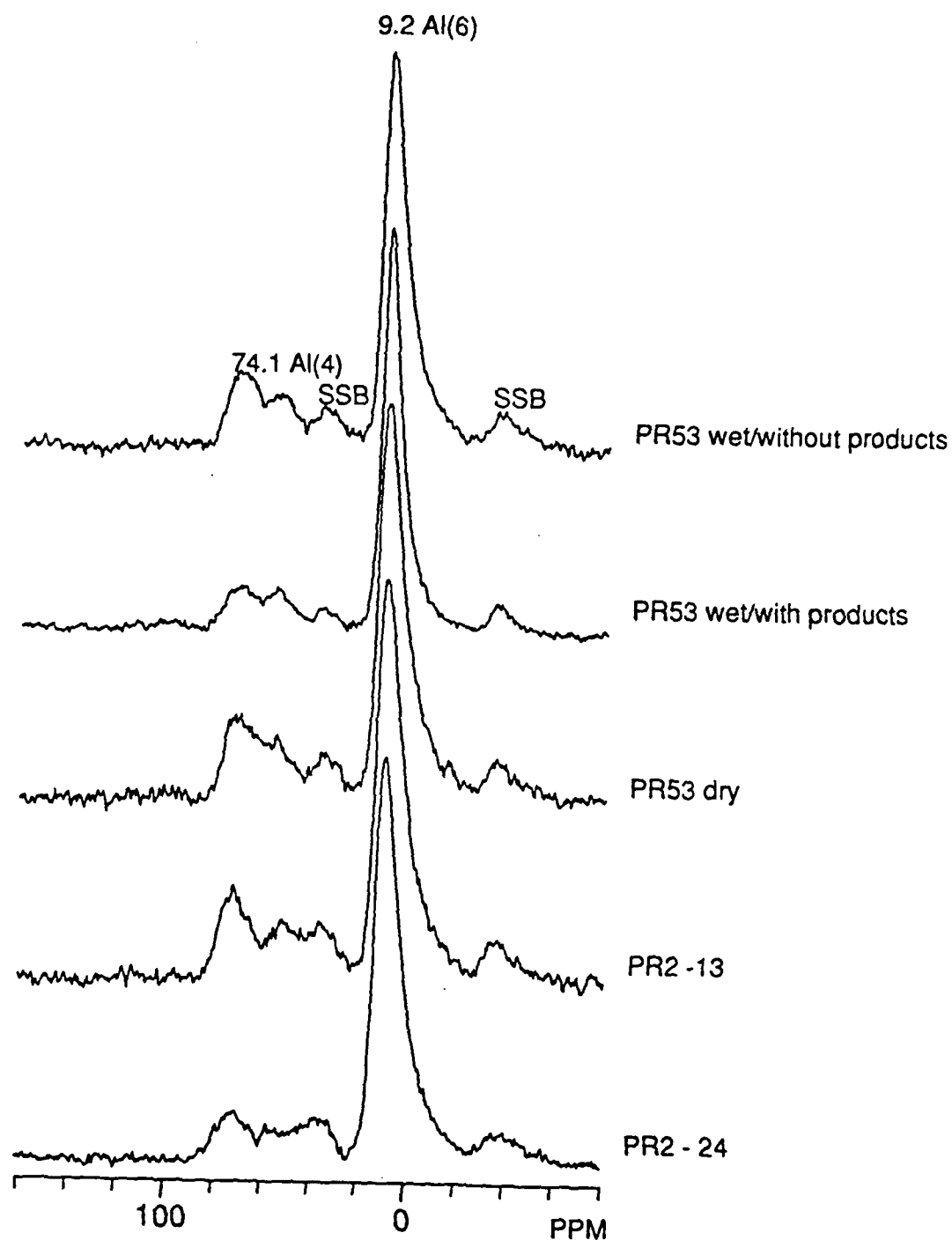
Figure 24. ^{27}Al CPMAS NMR spectra of MDF cements. (Sample PR2-13 contains boric acid and sample PR2-24 contains an epoxy-functional silane).

observed NMR spectra; that the extent of reaction is small (as expected); and that there is a relatively large amount of Al(4) in the hydrated phase. This hydrated Al(4) is at a less positive chemical shift than CA, and is probably present as amorphous material. Since an Al(4) hydrated species was not observed in the pure cements, it may be associated with a PVA-aluminate product. These spectra also illustrate well the importance of the CPMAS method, because the hydrated Al(4) is present at such a low concentration that it is undetectable in the MAS spectra and also would not be detectable by XRD.

2.11 Summary of Research Findings

The first three years of the Center have provided a solid base for an extended interdisciplinary research effort at the University of Illinois. There is still much to learn, but certain achievements demonstrate the success of the program.

Macro-Defect-Free Cements: The processing of MDF cements is now recognized as being critical to the performance of the composite. Lamination defects occur during the calendering step as the polymer gel gradually loses plasticity. Polymer-polymer diffusion, cross-linking and rheological changes all contribute to the problem. The development of polymer-polymer interfaces have been investigated in terms of the dynamics of interdiffusion of polymer chains and fractal analyses. These studies are of general interest to polymer scientists. The importance of cross-linking kinetics has been demonstrated qualitatively and quantitative studies are planned for the future. Similarly, rheological studies are scheduled for more detailed study.

Progress has also been made in understanding the moisture sensitivity of MDF cement, although the object of producing a fully water-resistant material has not been fully realized. Water is adsorbed by a molecular diffusion process through the polymer matrix. This water adsorption swells and softens the polymer. However, it has been observed that the strength of the hydrated cement matrix is also significantly reduced by adsorbed water. Since ionic cross-linked PVA in the MDF matrix is not water resistant the use of coupling agents has been explored. These can improve the polymer-cement interface as well as provide cross-linking action. This strategy has proved successful to the extent that it has been possible to produce MDF cement that is stronger after soaking in water for two weeks than the dry material produced by ICI. Nevertheless a strength reduction of 15-30% still occurs. Processing problems alluded to above seem to be a limiting factor at present.

Finally studies of cement hydration in the presence of polymers has shown that they have an important influence on the growth processes and the stability of hydrated phases. In this respect solid state NMR has been used for the first time to quantitatively determine reaction kinetics of hydration processes by in situ studies.

<u>DSP Cements</u>: Processing of DSP cement pastes was also found to be critical for optimized performance. The critical features were found to be complete dispersion of the silica fume and elimination of entrapped air voids. Once these were solved the maximum compressive strength of the pastes was 30,000 psi at 28 days and this was largely independent of silica fume content. Only about one third of the cement is able to hydrate, the rest behaving as a microaggregate.

The porosity of the paste is predominantly the intrinsic microporosity of the C-S-H binder. However, this is difficult to measure accurately since the pore structure is changed as water is removed before pore structure measurements can be made: microporosity is converted to mesoporosity. The best method is replacement of water by methanol followed by critical point drying. It also appears that a significant fraction of the microporosity can not be measured by nitrogen adsorption since it is too small to be penetrated by the nitrogen molecule. Water however can be adsorbed and negatively affect electrical properties. DSP cement pastes are good insulating dielectrics as long as they are kept dry. But at low relative humidities penetration of water into the micropores creates a conducting pathway which significantly degrades the electrical properties.

Curing at higher temperatures should increase the crystallinity of the binding phases and reduce the microporosity. Studies of under autoclaving conditions up to 240°C under saturated steam pressures has established the phases that can form. These processing conditions will be used for further studies on electrical properties.

Specialized Cement Systems: The study of fiber reinforced MDF cements was also initially plagued by processing problems. It was found that fibers could not survive the regions of the roll-milling undamaged, least of all the SiC fibers chosen to investigate the role of the interface. Eventually satisfactory lamination of a 1-dimensional array of aligned fibers between MDF layers was achieved. Changes in surface chemistry of the fiber were attained by various chemical and thermal treatments and the interfacial characteristics were examined using the nanoindenter at Oak Ridge National Laboratory. Although interfacial shear strengths in most cases were greater than the loading capacity of the indenter the observed trends were in agreement with anticipated behavior. The study indicates that good fiber-matrix binding can be anticipated in MDF laminates.

The studies on the magnesium phosphate cements have progressed to a promising point. The initial work on the monophosphate system revealed errors in published papers and a more reasonable chemical reaction was established. The latter work on the triphosphate system established that the triphosphate moiety is retained during hydration, as was anticipated. This system shows unusual rheological properties prior to setting, which can be used to advantage to create stronger bodies of lower porosity.

The development of "organoceramics" is looking very promising. This work, which is closely related to the MDF study, is attempting to form calcium aluminate hydrates containing ionic polymers. The basic chemistry has now been elucidated and crystals containing polymers have been obtained. Preliminary results suggests that the confined polymers do indeed contribute to an enhancement of mechanical properties, as was originally postulated. Further work is needed to determine the specific way in which polymers are held within the crystals and the strength of their interactions.

Setting of Cement: This project has used model suspensions of uniformly sized particles to study particle interactions and their effect on rheological behavior. Work has concentrated on response to small shear stresses below and just above the yield stress. At high particle volume fractions, approaching 0.60 the particles order into a well-defined lattice arrangement, forming a gel. Applying increasing shear stress to this gel, results in changing response. Elastic response, is replaced by viscoelastic behavior with a well-defined viscosity. but in an intermediate stress range a sluggish non-equilibirum viscoelastic response was observed, indicating that the yield stress is not a discontinuous point. At high stresses the viscosity dropped sharply. These behaviors have been interpreted in terms of particle pair interactions and packing geometries. This work has attracted a lot of attention from others working in the field.

3. Dissemination of Research Results

3.1 Theses

The following theses have been completed during the year.

S.A. Touse, "Microstructural Characterization of DSP Pastes", M.S. in Ceramic Engineering, May 1989.

J. A. Shunkwiler, "Influence of Moisture on the Structure and Properties of Macro-Defect-Free Cement Paste", M.S. in Ceramic Engineering, May 1989.

R.F. Falkner, "Processing of Portland Cement Macro-Defect-Free Composites", M.S. in Ceramic Engineering, August 1989.

H. Zhang, "Concentration Profiles at Amorphous Polymer-Polymer Interface." Ph. D. in Materials Science, October 1989.

This brings the total number of completed theses to six. The abstracts of all theses are reproduced in Appendix A.

3.2 Publications

Papers published or accepted during 1989 are listed below.

H. Zhang and R.P. Wool, "Concentration Profile for a Polymer-Polymer Interface, No. 1 Identical Chemical Composition and Molecular Weight." Macromolecules, 22 3018 (1989).

P. Messersmith and S.I.Stupp, "Novel Organoceramics: Polymers within Inorganic Crystals", Bulletin of the American Physical Society, 34 708 (1989).

S.A. Touse, T.A. Bier, C.A. Knepfler, J.F. Young and R.L. Berger, "Pore Structure of Low Porosity Cement Pastes" Materials Research Society Symposium Proceedings, 137 235-241 (1989).

J.F. Young, R.L. Berger and T.A. Bier, "Microstructure and Macroscopic Properties of Advanced Cementitious Materials" Festschrift Volume in honor of Professor Hilsdorf, Universitat Karlsruhe, in press (invited paper).

H.C. Chen and C.F. Zukoski,"Flow of Ordered Latex Suspension; Yielding and Catastrophic Shear Thining", Journal of the Faraday Society, accepted.

H.C. Chen and C.F. Zukoski, "Discontinuous Shear Thinning in Ordered Suspensions", Physical Review Letters, submitted.

The total number of publications for the three year contract are   . However, it expected that several more will be published over the next two years.

3.3 Conference Presentations

Oral presentations at several conferences and technical meetings have been given throughout the year, and these are listed below.

Fall Meeting of the Materials Research Society, November 1988; Symposium P - Pore Structure and Permeability of Cementitious Materials:

> S.A. Touse, T.A. Bier, C.A. Knepfler and J.F. Young, "Pore Structure of Low Porosity DSP Cement Pastes."

Society of Rheology Meeting, February, 1989:

> H.C. Chen and C.F. Zukoski, "Discontinuous Shear Thinning in Ordered Latex Suspensions".

American Physical Society Meeting, March 1989:

> P.Messersmith and S.I. Stupp, "Novel Organoceramics: Polymers within Inorganic Crystals."

American Ceramic Society Annual Meeting, April 1989:

> D.Hansen, J.Homeny and S.D. Brown, "SiC Fiber/ Macro-Defect-Free Cement Composites."

> M.C. Wagner, W.G. Klemperer and J.F. Young, "Investigation of the Structural and Chemical Properties of Cement Pastes Derived from the MgO-Polyphosphate-H_2O System."

> S. Touse-Shunkwiler, G. Sun and J.F. Young, "Silicate Polymerization of DSP Pastes."

> J. M. Bukowski and R. L. Berger, "Reactivity of Alkaline Earth Silicates to Carbon."Dioxide, and Water Vapor as Determined by Trimethylsilylation".

> T.A. Bier, G.Sun and J.F. Young, "The Influence of Drying Method on the Microstructure of Hydrated Cement Pastes."

> S. Touse-Shunkwiler, T.A. Bier, C.A. Knepfler and J.F. Young, "Physical Properties of DSP Pastes."

> J. Shunkwiler and J. F. Young, "Influence of Moisture on the Structure and Properties of Macro-Defect-Free Cement Paste."

> J. M. Bukowski, G. K. Sun and R. L. Berger, " A Study of Carbonated Calcium Silicates by Solid State Silicon-29 Nuclear Magnetic Resonance Spectroscopy."

3rd. Joint ASCE/ASME Mechanics Conference, July 1989:

> D.Hansen, J.Homeny and S.D. Brown, "SiC/Macro-Defect-Free Composites."

> M.Berg and J.F. Young, "Moisture Resistant MDF Cements."

Gordon Research Conferences, Summer 1989:

Chemistry of Interfaces:
C.F. Zukoski, "Rheology of Suspensions Near Close Packings" (invited talk).

Polymer Colloids:
S. Granick, "Nanometer-scale Properties Surfaces and Interfaces" (invited talk).

Fall Meeting of the Materials Research Society, November 1989; Symposium Y - Cements for Special Uses:

J.F. Young, "A Review of Macro-Defect-Free Cements".

M.Berg and J.F. Young," MDF Cements with Improved Water Resistance."

R.F. Falkner and J.F. Young, " Portland Cement-Based Macro-Defect-Free Composites."

4. Personnel

Additional faculty joined the Center when funding from NSF became available. There are now 16 faculty members in addition to Professors Young and Berger. The faculty Associates are listed in Table 11. Only 8 were actively directing projects supported by AFOSR funds during the past year.

Tables 12 and 13 list the graduate research assistants and research associates that have been working on center projects during 1988/89. Dr Bier also manages the laboratory facilities.

4.1 Awards

Center personnel have received the following awards during the year.

| J.F. Young | Elected a Fellow of the American Concrete Institute |
| D.A. Payne | Mitsui Toatso Chair in the Research Center for Advanced Science and Technology, University of Tokyo, Fall 1989 |

4.2 Other Activities

Other noteworthy activities by Center personnel are listed below.

C.F. Zukoski	Invited speaker at the Gordon Conference on Chemistry of Interfaces
S. Granick	Invited speaker at Gordon Conference on Polymer Colloids
J.F. Young	Member, Steering Committee for Conference on Advances in Cementitious Materials, July 1990

Table 11 - Listing of Faculty Associates

Name	Departmental Affiliation	Research Interests
M. Berg*	MSE-Ceramics	Ceramic processing
S. D. Brown*	MSE-Ceramics	Fracture testing
R. C. Buchanan	MSE-Ceramics	Alumina phosphate cements
S. Granick	MSE-Polymers	Polymer-solid interfaces
J. Homeny*	MSE-Ceramics	Fracture of composites
R. J. Kirkpatrick*	Geology	Mineral structures
W. G. Klemperer*	Chemistry	Synthesis of metal-oxygen structures
G. Kordas	MSE-Ceramics	Electron paramagnetic resonance
W. M. Kriven	MSE-Ceramics	Electron microscopy Microstructural characterization
A. J. McHugh	Chemical Engineering	Polymer processing
D. A. Payne	MSE-Ceramics	Electrical properties Ceramic processing
L. J. Struble	Civil Engineering	Rheology of cements Computer modelling
S. I. Stupp*	MSE-Polymers	Polymer-ceramic interfaces
C. L. Tucker	Mechanical Engineering	Polymer processing
R. Wool*	MSE-Polymers	Polymer interfaces
C. F. Zukoski*	Chemical Engineering	Properties of colloids

*P.I. or Co-P.I. of an AFOSR supported project

+MSE = Materials Science and Engineering

Table 12 - <u>Graduate Research Assistants Employed During 1988/89</u>

Name	Project #	% time	Date Appointed	Last Degree & Institution & Date	Degree
P. Russell	21	50	10/29/86	B.S., Ceramic Engr. U. Missouri-Rolla, 1979	M.S.
R. Desai	21	50	8/20/88	B.S., Ceramic Engr. Rutgers U.	MS.
D. Hansen	23	50	5/20/87	B.S., Ceramic Engr. U. Illinois, 1987	M.S.
A. Burreson	23	50	8/20/88	B.S., Ceramic Engr. U. Washington, 1988	M.S.
P. Messersmith	24	25	8/20/87	B.S., Bioengr. Clemson U., 1987	B.S.
H. Zhang	26	50	8/20/87	B.S., Radiation Chem. U. Sci. Technol. of China Beijing 1969	Ph.D.
J. Shunkwiler	28	50	8/20/87	B.S., Ceramics Ohio State U., 1987	M.S.
S. A. Touse	28	50*	8/20/87	B.S., Ceramic Engr. Ohio State U., 1987	M.S.
L. B. Chen	29	50	5/20/87	M.S. Chem. Engr. U. Illinois, 1988	Ph.D.
X-D. Cong	30	50	8/20/88	B.S.	Ph.D.

*Not supported by Center funds.

Table 13 - <u>Research Associates Supported by the Center</u>

Name	Qualifications	Year Graduated
Th. A. Bier	Ph.D., Civil Engr. Materials U. Karlsruhe, W. Germany	1987
G. K. Sun	B.S., Silicate Chemistry U. Nanjing, China Academy for Building Materials, Beijing, China	1956
M. Wagner	Ph.D., Chemistry Virginia Tech	1987

5. Facilities

The major items of equipment obtained by the Center are itemized in Table 14. These instruments form a laboratoy facility for the characterization of powders and porous materials. The facility supports the Centers program and is available on a priority basis to its faculty and students at a modest fee to cover expendible materials and some maintenance costs. The facility is also available to others in the University at slightly higher charges in order to build up reserve funds for more costly maintenance. An analysis of use of the instruments acquired in 1987 is given in Figure 25. Limited use of the faclity is provided to the Industrial Affiliates at favorable rates.

In looking at these figures it should be remembered that the SEM is a joint facility with the Advanced Construction Technology Center. Also particle size distribution analyses can be made with one of two instruments. One of these belongs to the Department of Materials Science and Engineering, but is part of the Center facility.

6. Other Activities

6.1 Annual Technical Review

The Center is planning a final technical review on February 5 and 6, 1990 at the University. The first half day will be devoted to presentations by the Faculty Associates on the status of their research programs. The second half day will include meetings of the Advisory Committee and the Industrial Affiliates Board. Invitations have been sent to selected personnel from Air Force Laboratories.

6.2 Advisory Committee

The Advisory Committee was appointed in 1987, to offer advice concerning the ongoing research programs and future directions. The members are listed in Table 15. The advisory committee will be disbanded after this meeting. A similar advisory function has been set up for the NSF - funded interinstitutional ACBM Center.

6.3 Industrial Affiliates Program

In March 1988 a group of companies were invited to campus to visit the Center. A day long program was set up which included an overview of the Center's research programs, a tour of the facilities, and the presentation of a proposed industrial affiliates program. Seventeen companies were represented at the meeting and subsequent enquiries resulted in individual visits by another 4 companies.

Table 14 - Major Equipment Purchased by the Center

Instrument	Supplier & Model	Remarks	Year Acquired
2-roll mill	Stannant	Used model	1987
Mercury Porosimeter	Micromeritics Model 9220	Four low pressure and two high pressure stations	1987
Nitrogen Adsorption	Micromeritics Model ASP 2400	Six adsorption stations and six outgassing stations	1987
X-ray/Image Analysis System (for SEM)	Princeton-Gamma-Tech, System 4	Interfaced with an Hitachi SEM, Model S-530	1987
X-ray Diffractometer	Rigaku, Model Geigerflex Dmax-II		1987
Particle Classifier	American Alpine Model 100 MZR		1987
Small Strain Creep Apparatus	Bohlin Rheologi	With air-table for isolation from vibrations	1987
Particle Size Analyzer	Horiba, Model CAPA700	100-0.01 µm size range	1987
UV-VIS Spectrophotometer	Cary, Model 2200		1988
Size Exclusion Chromatograph	Waters	Modular package	1989
Attritor Mill	Union Process, Model		1989
Mechanical Testing Equipment	Instron, Model 4500	Funds provided by the University	1989

Table 15 - Advisory Committee Members

Name	Affiliation	Location	Term
Prof. Sidney Diamond (Chairman)	School of Civil Engr. Purdue University	West Lafayette, IN	1987-89
Dr. G. J. C. Frohnsdorff	Div. of Bldg. Materials N.I.S.T.	Gaithersburg, MD	1987-89
Captain Konrad Felice	Air Force Weapons Lab	Kirtland AFB, NM	1987-88
Dr. Rod Galloway	Air Force Weapons Lab	Kirtland AFB, NM	1988-89
Major J. W. Hager	Electronic & Mater. Sci. AFOSR	Bolling AFB, DC	1987-88
Dr. Liselotte Schioler	Electronic & Mater. Sci. AFOSR	Bolling AFB, DC	1988-89
Mr. Alan Koblin	CEMCOM Research Associates	Lanham, MD	1987-89
Mr. C. S. Saunders	Composite Mater. Group ICI Advanced Materials	Washington, DC	1987-89

An affiliates program was officially launched in August 1988, and in 1989 there were seven members:

> Relmech Manufacturing Co., Elmira, Ontario, Canada
> Weyerhaueser Corp., Tacoma, WA
> Cemcom Corp., Lanham, MD
> Hi-Tek Polymers, Louisville, KY
> Nalco Chemical Co., Naperville, IL
> W. R. Grace & Co., Columbia, MD
> Portland Cement Association, Skokie, IL

The affiliates program has been folded into a larger program set up for the NSF Center and starting in 1990.

Appendix A
Abstracts of completed theses

ABSTRACT

Macro-defect-free (MDF) composites were processed by high-shear mixing on a twin roll mill using commercial Portland cements and a poly(vinyl aclohol)/acetate copolymer. Laminations in the cured composites limited flexural strengths to around 100 MPa. Several methods were tried to remove the laminations, including pre-hydrating of the cement, adding retarders, modifying the cement by removal of reactive fine particles, using alite or belite, substituting silica for some of the cement, and controlling the temperature of the process. The laminations could not be removed without inhibiting the cross-linking of the PVA. The addition of 0.40 g EDTA was the only method which reduced the laminations to reasonably acceptable levels.

Evidence from processing and solution chemistry suggests that these laminations are caused by the precipitation of the polymer on the surface of the composite during high shear mixing. Calcium silicate cements also exhibited higher concentrations of Ca^{2+} than the calcium aluminate cement. The precipitation is thought to be caused by the high alkalinity of Portland cement solutions, the high temperatures encountered during shear mixing of the cement, and the rapid cross-linking of the cement by the high concentration of Ca^{2+} ions released by the cement. It was concluded that commercial Portland cements could not be used to produce high strength macro-defect-free composites equal to those made with a calcium aluminate cement.

INFLUENCE OF MOISTURE ON THE STRUCTURE AND PROPERTIES OF MACRO-DEFECT-FREE CEMENT PASTE

Jeffrey A. Shunkwiler, M.S.
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign, 1989

The influence of wet/dry cycling on the moisture absorption, dimensional change, and flexural strength of Macro-Defect-Free (MDF) cement paste made from calcium aluminate cement and partially hydrolysed polyvinyl alcohol was investigated as a function of relative humidity. Unmodified and crosslinked compositions were studied. A linear relationship was found to exist between moisture absorption and dimensional change for both wetting and drying. When large amounts of moisture were absorbed, wet strengths were significantly lower than dry strengths, but when only limited amounts of moisture were absorbed, the opposite was true. This behavior was attributed to the hygroscopicity and swelling properties of the polymer used. Removal of the polymer from the MDF composite resulted in a 95% loss of flexural strength, from 250 MPa to 15 MPa, which was partially recovered (to 80 MPa) upon rehydration of the cement. Fourier Transform-Infrared (FT-IR) spectroscopy studies of the cement, polymer, and MDF composite are presented.

MICROSTRUCTURAL CHARACTERIZATION OF DSP PASTES

Sara Ann Touse, M.S.
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign, 1989

DSP cement pastes were prepared using white Portland cement (PC), amorphous silica fume, and a superplasticizer. The fume/cement ratios varied from 0.06 to 0.36, and the samples were cast using vibration. The water/powder ratio used was 0.18. The pore structure, compressive strength, silicate polymerization, and chemical composition were studied.

The measured pore volumes and specific surface areas are reduced in *DSP compared to superplasticized PC pastes without silica fume.* This is due to a reduction in the amount and size of porosity formed in DSP. Specific surface areas measured decrease beyond 3 days hydration indicating a tightening of the pore structure.

Silicate polymerization was studied by trimethylsilylation. The maximum degree of hydration was roughly 30% due to the low water contents used in these pastes.

Compressive strength values were 22,000 psi at 28 days. The data follows a Ryshkewitch equation with σ_o equal to 26,900 psi and k equal to 3.5. Compressive strength, porosity measured by mercury porosimetry, and degree of hydration were all found to be independent of silica fume content.